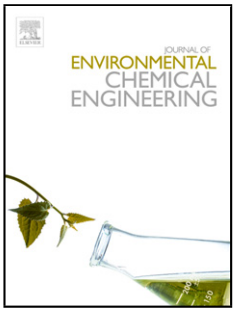
Accepted Manuscript



Title: Insight into Wastewater Decontamination Using Polymeric Adsorbents

Authors: Peter Adeniyi Alaba, Nurudeen Abiola Oladoja, Yahaya Mohammad Sani, Olumide Bolarinwa Ayodele, Isah Yakub Mohammed, Sunday Felix Olupinla, Wan Mohd Wan Daud

PII: S2213-3437(18)30091-5
DOI: https://doi.org/10.1016/j.jece.2018.02.019
Reference: JECE 2211

To appear in:

Received date: 27-10-2017
Revised date: 7-2-2018
Accepted date: 12-2-2018

Please cite this article as: Peter Adeniyi Alaba, Nurudeen Abiola Oladoja, Yahaya Mohammad Sani, Olumide Bolarinwa Ayodele, Isah Yakub Mohammed, Sunday Felix Olupinla, Wan Mohd Wan Daud, Insight into Wastewater Decontamination Using Polymeric Adsorbents, Journal of Environmental Chemical Engineering https://doi.org/10.1016/j.jece.2018.02.019

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

ACCEPTED MANUSCRIPT

Insight into Wastewater Decontamination Using Polymeric Adsorbents

Peter Adeniyi Alaba[1]*, Nurudeen Abiola Oladoja[2], Yahaya Mohammad Sani[3], Olumide Bolarinwa Ayodele[4], Isah Yakub Mohammed[5], Sunday Felix Olupinla[6], Wan Mohd Wan Daud[1]

[1]*Department of Chemical Engineering, Covenant University, P.M.B 1023, Sango-ota, Ogun-State, Nigeria.*

[2]*Department of Chemical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia*

[3]*Department of Chemical Science, Adekunle Ajasin University, Akungba, Akoko, Nigeria.*

[4]*Department of Chemical Engineering, Ahmadu Bello University, 870001, Nigeria.*

[5]*Department of Chemical Engineering, Universiti Teknologi Petronas, 32610, Bandar Seri Iskanda, Perak, Malaysia.*

[6]*Department of Chemical Engineering, Abubakar Tafawa Balewa University, P.M.B. 0248, Bauchi, Nigeria.*

[7]*Department of Petroleum and Natural Gas Processing Engineering, Petroleum Training Institute, Effurun, Delta State.*

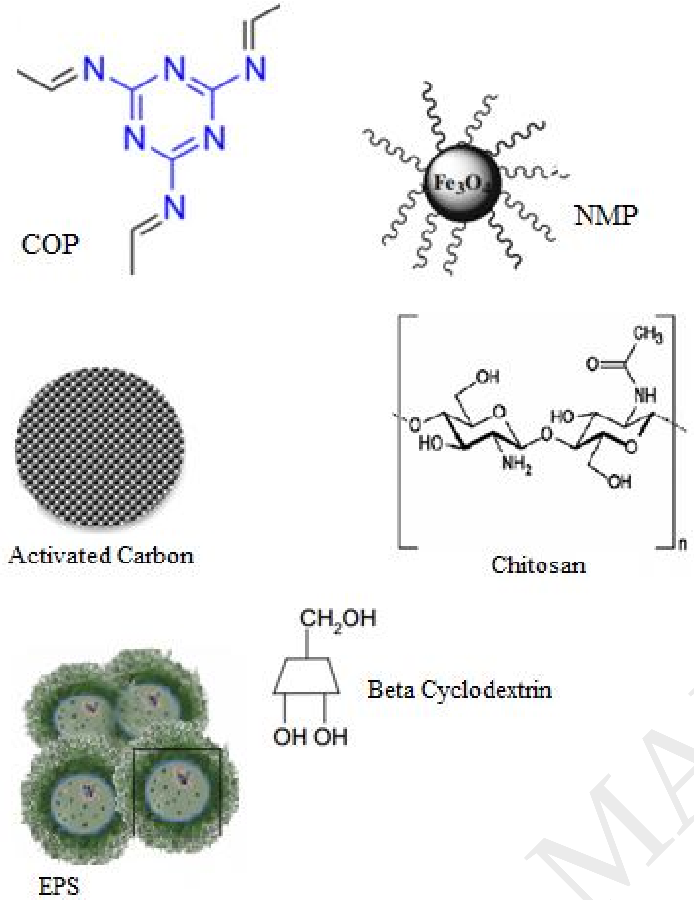
*Correspondence: Tel.: +2348186628769;

Email: adeniyipee@live.com (P.A. Alaba).

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Graphical Abstract



Polymeric adsorbent: a suitable and cost effective alternative to conventional Activated carbon

Highlights

- High cost of activated carbon is the major drawback preventing its industrialization.
- Polymeric adsorbents pose a suitable inexpensive alternative to activated carbon.
- NMPs exhibit facile separation in solid–liquid system without further separation.
- Polysaccharides exhibit remarkable selectivity for metals and aromatic compounds.
- COPs exhibit a similar potency to that of AC inspite of their moderate surface area.
- EPS provides binding sites for metals due to the availability of charged moieties.

ABSTRACT

The use of polymeric adsorbent for decontamination of various sources of water was critically reviewed. This arises from the alarming increase in water scarcity in many parts of the world due to increase in population, which exerts

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

immense pressure on the available water resources. Treatment of wastewater, stormwater and seawater via series of technological pathways like adsorption, desalination, advanced oxidation and solid-phase microextraction constitute new strategies for removal of toxins, antibiotics, complex matrix samples, and heavy metals for sustainable production of potable drinking water. This study reviewed the use of polymeric adsorbents such as nano-magnetic polymers (NMPs), polysaccharides, extracellular polymeric substances (EPS), and covalent organic polymers (COPs) for effective decontamination of water. These materials were critically analyzed with emphasis on their characteristics, strengths, drawbacks, as well as the enhancement techniques. Furthermore, the mechanisms of adsorption involved were also discussed. This review shows that polymeric adsorbents have demonstrated remarkable removal efficiency for several contaminants.

Keywords: Nano-magnetic polymers; Chitosan; Cyclodextrin; Covalent organic polymers; Extracellular polymeric substances; Wastewater treatment.

Table of Contents

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

1. Introduction

Non-biodegradable contaminants found in wastewater and sludge such as dyes, phosphorus, sulfamethazine and heavy metals, which commonly have a density < 5 g/cm^3 and atomic weights ranging from 63.5 to 200.6 [1]. Water pollution associated with release of these contaminants to the atmosphere has been a major environmental concern worldwide [2]. The contaminants abound in the wastewaters released from modern chemical industries such as textile, dyestuffs, metal plating, paper, mining, fertilizer, battery manufacturing [3], metallurgical, pesticides, fossil fuel, tannery, mining and various plastics like polyvinyl chloride. The release of these contaminants into environment have been increased extensively by the recent rapid industrialization [2]. Since they are not easily biodegradable and some completely non-biodegradable these contaminants tend to accumulate in living organisms as, unlike the organic types that are easily biodegradable [3]. These toxic contaminants commonly found in treatment of industrial wastewaters include dyes, zinc, chromium, phosphorous, sulfamethazine, copper, mercury, nickel, arsenic, cadmium and

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

lead. The occurrence of little quantities (< 1 ppm for some dyes) of dyes in water is highly noticeable and detrimental. Generally, about 2% of dyes produced form industries are directly discharged in wastewater [2]. Wastewater generated from dyestuffs must be treated to eliminate dyes before they are discharged to the ecosystem because of the stringent restrictions on the organic content of the wastewater. Many of these dyes are hazardous, posing a severe hazard to aquatic life due to their toxicity and carcinogenicity. However, treating wastewater-containing dyes is arduous, because dyes are not degradable by aerobic digestion, recalcitrant organic matter, and are stable to oxidizing agents, light and heat [2].

Several authors have comprehensively investigated the toxicity of heavy metals such as lead, cadmium, zinc, mercury, chromium and arsenic on human wellbeing [3]. Their reports indicate that high blood pressure, memory loss, aggressive behavior, vascular occlusion, mood swings, autoimmune diseases, fatigue, irritability, speech disorders, poor concentration, increased allergic reactions, depression, and sleep disabilities are the possible symptoms of heavy metal toxicity [4]. These toxic metals can also disturb the human cellular enzymes, running on nutritional minerals like selenium, zinc, and magnesium. Heavy metal such as mercury, lead, arsenic and cadmium are unsafe for human life [5]. Although, heavy metals such as zinc, iron, copper, chromium and manganese are essential for our human body, certain quantities of these metals are exceptionally harmful [6].

Phosphorus is known to be one of the foremost dissolved nutrients of eutrophication in natural waters [7]. Phosphorus finds its way to the water body from human waste, cow manure, lawn fertilizer, overflow the land into lakes and rivers to promote growth of plants such as algae, thereby declining the amount of dissolved oxygen in the water body, resulting in the death of mollusks and

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

fishes. Removal of this contaminant from the water body will solve this problem and help to meet the future sustainability of phosphorous resources [7].

Presently, the treatment of wastewater containing the above-mentioned contaminants is by combination of activated carbon (AC) adsorption and biological treatment. Despite the fact that commercial AC is a prominent adsorbent for dyes and heavy metals removal, its industrial application is stalled due to exorbitant cost [8, 9]. Recently, several techniques have been investigated towards developing inexpensive and effective adsorbents. Several researchers have proposed a number of non-conventional cheap adsorbents, which include biosorbents, natural materials, and agricultural and industrial waste materials [10]. These sorbents materials are capable of removing heavy metals and dyes from wastewater. They include siliceous material (perlite, alunite, silica beads), zeolites, clay materials (kaolinite, bentonite) [11], industrial waste products (metal hydroxide sludge, waste carbon slurries), agricultural wastes (coconut shell, rice husk, maize cob, bagasse pith), biosorbents (cyclodextrin, starch, chitosan, biomass, cotton, peat) [12]. Furthermore, the widely used inexpensive technique for phosphorous removal from wastewater is enhanced biological phosphorus removal (EBPR) [13]. This removal process is undertaken by a group of selectively enhanced heterotrophic bacteria known as phosphorus accumulating organisms (PAOs), which excessively takes up phosphorus. Extracellular polymeric substances (EPS), which usually form a matrix at the enclosure of the microbial cells or outside the cells play a vital role in the removal process [14].

Polymeric adsorbents include nano-magnetic polymers (NMPs), polysaccharides (such as chitosan and cyclodextrin), extracellular polymeric substances (EPS), and covalent organic polymers (COPs), which are confirmed inexpensive and readily available [15-18]. One of the unique feature of NMPs is rapid solid-liquid separation and remarkably minimizes the pre-treatment time [19]. It

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

has ability to swiftly and accurately determine trace environmental pollutants like phenols and heavy metal ions [19, 20]. Polysaccharides have a number of intrinsic characteristics, which make them effective towards removal of contaminants. Prominent among the attributes include low-cost and availability, their outstanding complexation and chelation capability. Their suitability is based on ability to tightly bind contaminants, particularly heavy metal ions [8]. COPs are exceptionally stable in several harsh conditions like high temperatures even in boiling water [21], and are confirmed promising for environmental applications such as groundwater remediation [22], and solvent uptake [23]. EPS play vital roles in common biological wastewater treatments such as membrane bioreactors (MBRs), activated sludge processes and fixed-film processes. It significantly affects the dewaterability floc size and stability, settleability and flocculability for flocs and sludge retention and biofilms shear resistance [24, 25].

This article reviews the technical feasibility of the above mentioned polymeric adsorbents for removal of various contaminants from wastewater [17]. It provides an insight into the use of polymeric adsorbents for effective decontamination of wastewater. These materials are critically analyzed, describing their characteristics, advantages and limitations. Furthermore, the mechanisms of adsorption involved will be discussed. This review shows that polymeric adsorbents have demonstrated remarkable removal efficiency for several contaminants.

2. Environmental Impact of Contaminants

2.1. Heavy metals

Different heavy metals such as Cd, Cu, Ni, Mn, Pb, Cr, and Zn, may be found in wastewater depending on the source. Accumulation of heavy metal in the soil and vegetables maybe due to incessant irrigation of agricultural land with industrial wastewater and sewage [26].

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Heavy metals are harmful because of their anthropogenic environmental impacts. Irrigation of wastewater results in heavy metals accumulation in foodstuff brings about impending health risks to consumers [26]. The concentration of heavy metal in plants grown in wastewater-irrigated soils were considerably higher ($P <= 0.001$) than in plants grown in the reference soil, and surpassed the tolerable limits according to the World Health Organization [27] and the State Environmental Protection Administration (SEPA) recommendation in China [28].

Soils are the basic and most vital part of the ecological system and are also severely contaminated. Hitherto, above 20,000,000 acres of farmland in China have been polluted by heavy metals like Zn, Cr, Pb, and Sn, which account for about 20% of the total farmland area suitable for growing crops. China undergoes a 10,000,000 tons' loss of crop output yearly because of weakening heavy metal pollution [29]. Unlike other organic contaminants, harmful heavy metals are indestructible since they are not biologically or chemically degradable. Additionally, certain heavy metals could concentrate along the food chain and finally amass in human body being at the top of the food chain [30]. Therefore, increasing attention is required to prevent heavy metal contamination being the root of soil pollution.

2.2. Dye

The presence of dyes in wastewaters in the company of other lingering chemical reagents used for processing have created significant complications in the treatment of wastewater [31]. Textile wastewaters exhibit high organic content, as well as low BOD/COD ratios (< 0.1) because dyes are not biodegradable in nature [32]. The textile wastewater treatment plants generated final effluent always displays a definite degree of colour intensity. The coloured waste disposal to receiving waters is visually unpleasant, to say the least [31]. More than 50000 metric ton of dye is released into textile effluent yearly, with various types of dye in varying proportion based on the

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

relative degree of dye fixation, the fibre of application, and dye type [33]. Although all dyes are not noxious compounds, a number of them could form aromatic amines, which are hazardous [31, 34]. Therefore, the potentially hazardous effect of some dye-contaminated water is a serious concern.

2.3. Phosphorus

Phosphorus is known to be one of the foremost dissolved nutrients of eutrophication in natural waters [7]. Phosphorus finds its way to the water body from human waste, cow manure, lawn fertilizer, overflow the land into lakes and rivers to promote the growth of plants such as algae, thereby declining the amount of dissolved oxygen in the water body, resulting in the death of mollusks and fishes. Removal of this contaminant from the water body will solve this problem and help to meet the future sustainability of phosphorous resources [7].

3. Nano-magnetic polymers (NMPs)

NMPs have gained the attention of many researchers due to their numerous technological applications such as magnetic storage media, targeted drug delivery [35], magnetic inks for jet printing contrast agents in magnetic resonance imaging, and biosensing applications [35]. Their applications have also been extended to removal of heavy metal, where they exhibit ability to enhance adsorption capacity and rate, as well as selectivity for targeted metal ions. They are cost effective and also exhibit inherent magnetic properties, which enable fast and facile solid–liquid separation under an applied magnetic field, without centrifugation or filtration [35]. However, magnetic nanoparticles are limited due to their susceptibility to air oxidation and ease of aggregation in aqueous systems [35, 36]. Some researchers have shown that ‘‘core–shell’’ structured nano-magnetic polymers (NMPs) could be a novel alternative adsorbents to bare magnetic nanoparticles [35].

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Core–shell structured NMPs are produced by coating the magnetic core (Fe_3O_4) with functional polymers to enhance the stability of nano-dispersions by inhibiting their aggregation. This has been proved novel adsorbents recently. On the other hand, since incorporation of functional groups typically exhibit a high complex capacity with heavy metal ions, resulting in superior chemical stability, adsorption rate, capacity, and selectivity for the target metals [35], it is essential to engraft magnetite nanoparticles with functionalized polymers to enhance their adsorption efficiencies [37]. This could help in removal of toxic metals such as Cr(VI) and Cu(II) from aqueous solutions [36]. However, rational design of a suitable ‘‘Core–shell’’ structured NMPs demands that the optimum ratio between magnetic core and shell must be determined. Since insufficient magnetic oxide (the core) could terminate magnetic response due to disorientation of the surface spin [35, 38], and insufficient polymer component (the ‘‘shell’’) could result in poor adsorption capacity [35]. Pan *et al.*, [35] reveals that the optimum composition of the magnetic (core Fe_3O_4) for mercapto-functionalized core–shell structured nano-magnetic Fe_3O_4 polymers is 5.88%. Shamim *et al.*, [39] prepared thermosensitive Core–shell structured NMP adsorbents by using N-isopropylacrylamide (NIPAM) as the polymer shell and surface modified Fe_3O_4 as the core. The essence of the surface modification is to ensure stability against agglomeration. The adsorbents were synthesized by using seed polymerization method and surface modified Fe_3O_4 particles as the seeds as shown in Scheme 1. The crosslinker used is N,N-methylene bis acrylamide to provide mechanical strength to the particles and the initiator is potassium persulfate. The thermosensitive adsorbent shows a high adsorption capacity when employed for separation of Bovine Serum Albumin (BSA).

Well prepared NMP adsorbents exhibit superparamagnetic properties as confirmed by almost zero coercivity [40] and remanence in their VSM magnetization curve (Fig. 1).

[Insert Figure 1]

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

To increase the maximum adsorption capacity (q_m) of NMPs, several functional groups such as carboxylate, phosphate, sulfate, hydroxyl, amino and amide groups, have been explored for modification of conventional adsorbents. The most effective ones for heavy metals removal is amino- functionalized NMPs.

3.1. Functionalized Fe_3O_4 magnetic polymers

3.1.1. Amino-functionalized Fe_3O_4 magnetic polymers

Although depending on the preparation method, modfying MPs with functional groups could be effective towards improving the q_m for heavy metals removal. For instance, the report of Huang & Chen [41] showed that amino-functionalized magnetic adsorbent, synthesized by the covalent binding of polyacrylic acid (PAA) on Fe_3O_4 particles surface prior to amino-functionalization (using diethylenetriamine (DETA)) using carbodiimide activation, gives the value of q_m (11.24 mg/g) for Cr(VI) removal. This is slightly lower than that reported by Hu *et al.*, [42] when they used maghemite nanoparticle (γ- Fe_2O_3). Zhao *et al.*, [43] prepared a series of ethylenediamine (EDA)-functionalized MPs (EDA-MPs) by suspension polymerization (copolymerizing glycidylmethacrylate (GMA), Methyl methacrylate (MMA), and divinylbenzen (DVB)) to form epoxyl-functionalized MP prior to functionalization with EDA using ring-opening reaction (Scheme 2). They reported that the value of q_m for Cr(VI) removal from wastewater varies with the amount of GMA in the core-shell structured EDA-MPs. The increases from 32.15 to 61.35 mg/g (Langmuir isotherm) with increase in GMA from 2 to 10 mL.

Furthermore, Zhao *et al.*, [44] also investigated the adsorption performance of Four kinds of NH_2-functionalized NMPs (NH_2-NMPs) with different amino groups of chromium(VI) ions removal.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

The adsorbents include tetraethylenepentamine [45], triethylentetramine (TETA), EDA, DETA, named as TEPA-NMPs, TETANMPs, EDA-NMPs, and DETA-NMPs, respectively. The value of q_m for the adsorbents are 370.37, 204.08, 136.98, 149.25 mg g^{-1}, for TEPA-NMPs, TETANMPs, EDA-NMPs, and DETA-NMPs, respectively [46]. The remarkable performance recorded here may be due to the nano size of the adsorbent, which offers higher adsorption sites compared to that of Zhao *et al*., [43]. The adsorption of Cr(VI) onto the NH_2NMPs follows a path associated with electrostatic attraction, ion exchange, and coordination interactions (Scheme 3).

Shen *et al.*, [36] investigated the effect of amino groups (EDA, DETA, TETA and incorporation on NMPs (NH2-NMPs) for removal of Cu(II) and Cr(VI) from water. Their result reveals that incorporation amino groups is crucial in adsorption of the metal ions, and the higher the amount of amino groups in the sample, the higher the value of q_m. They also reported formation of new adsorbents via adsorption of Cr(VI) or Cu(II) onto NH2-NMPs, designated Cr-NH2-NMPs (Cr-TEPA-NMPs, Cr-TETA-NMPs, Cr-DETA-NMPs, Cr-EDA-NMPs); and Cu-NH2-NMPs (Cu-TEPA-NMPs, Cu-TETA-NMPs, Cu-DETA-NMPs, Cu-EDA-NMPs), respectively [36] . Cr-NH2-NMPs and Cu-NH2-NMPs reusable for further removal of Cr(VI) or Cu(II) in a separate experiment, giving a remarkable selectivity, broad pH applicable range as well as comparable adsorption performance with that of NH2-NMPs. On the other hand, the value of q_m depends on the solution pH. The report of Pan *et al.*, [20] showed that NMPs adsorbent under acidic pH condition below 3.0 have a higher value of q_m than when in alkaline solution, when applying graphene oxide based magnetic polymer in adsorbing chlorophenols (CPs). This is because the acidic pH enables hydrogen bond (–C=O· · ·H) formation easily with the hydroxyl of CPs in molecular state at carbonyl (–C=O) site, and the hydrogen bond (–N–H· · ·Cl) and π– π interaction with GO sheets [19]. However, a weak electrostatic attraction was experienced between the

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

negatively charged CPs and NH_3^+ since the ionic state of CPs is low in the solution. Nevertheless, hydrogen bond formation with hydroxyl of CPs over NH_3^+ is challenging. Conversely, alkaline pH does not support hydrogen bond formation for both $–NH_2$ and –C=O since less hydroxyl are present in the deprotonated CPs, and the key driving forces for adsorption of CPs were the π– π interaction and hydrogen bond (–N–H· · ·Cl). The GO sheet has ample hydrophilic groups as well as carboxylic, hydroxyl, and epoxide groups on its surface [47, 48], which are also recorded for GMA [15]. Zhao *et al.*, [15] employed GMA as a functional monomer in the synthesis of core–shell nano-ring magnetic molecularly imprinted polymer functionalized with amino group. The integration of magnetic properties with GO synergistically combines the high q_m of GO with the convenience magnetic controllable separation as well as the high q_m of amine [49]. Figure 2 presents XPS spectra for functionalized Fe_3O_4 magnetic polymers for removal of Cr(VI) from wastewater.

The adsorption mechanism on NMP adsorbents functionalized with amino groups can be investigated using XPS. The study of Shen *et al.*, [36] confirmed this when they studied the adsorption mechanism of TEPA-NMPs for Cr(VI) and Cu(II) removal from wastewater. Their result was presented in Fig. 2. The main peak is found at ~932.6 eV (binding energy) and the peak at ~943.2 eV (Fig. 2(a)) is its satellite peak due to the presence of Cu $2p_{3/2}$, whereas the main peak at ~952.2 eV has its satellite peak at ~961.2 eV (Fig. 2(a)) due to the presence of Cu $2p_{1/2}$ [50]. The binding energy at ~397.4 eV, which corresponds to N1s (Fig. 2 (b) was ~2.6 eV lower than the energy of free NH_2 (~400 eV). This is attributable to the charge transfer between NH_2 and Cu(II) to generate NH_2Cu^{2+}. The binding energy of Cr $2p_{1/2}$ and Cr $2p_{3/2}$ found at 574.2 and 584.3 eV (Fig. 2(c)), may be due to the Cr(VI) adsorption onto Cu-TEPA-NMPs (the new adsorbent formed by adsorption of Cu onto TEPA-NMPs). Similarly, the binding energy peak at 166.7 eV

ACCEPTED MANUSCRIPT

(Fig. 2(d)), corresponding to S2p of SO_4^{2-}, becomes weaker as compared with that of Cu-TEPA-NMPs. This reveals that the SO_4^{2-} groups were virtually replaced by $HCrO^{4-}$ by via ion exchange interaction [36].

[Insert Figure 2]

2.1.2. Graphene oxide supported core-shell magnetic polymers

The outstanding propreties of graphene oxide (GO) such as strong mechanical strength, excellent thermal and electric conductivity, and high surface area, the oxidation state of graphene (G), has greatly enticed several researchers in the field of adsorption as well as solid phase extraction [51-53]. Moreover, GO has ultrahigh specific surface area and large delocalized π-electron system, making it a promising candidate with high adsorption capacity strong and affinity for carbon-based ring structures and non-polar compounds [54]. The use of GO as a support is promising in several technological fields such as hydrogen storage [55], sensor devices electronics [56], drug delivery [57], water treatment [20], and catalyst [58]. Therefore, GO can function as a solid-support substrate where the functional micro - or nano -particles of core-shell structured magnetic polymers were deposited or grown. However, it is essential to minimize the use of GO adsorption sites by the the functional micro - or nano –particles to avoid competition with the targeted adsorbate, and also ensure avoidance of GO sheets aggregation to optimize the adsorption capacity of the adsorbent [19]. Chen *et al.*, [47] rationally designed GO-based magnetic polymer (GO-Fe3O4@P) by employing combination of distillation precipitation polymerization, ring-opening and amidation reactions. The adsorption performance of the adsorbent was tested for removal of 2,4,6-trichlorophenol (2,4,6-TCP) in a batch adsorption system. The adsorption property of the absorbent significantly depends on pH and the value of qm was observed to be 232.6 mg/g. The adsorption pathway follows hydrogen bonding and π-π stacking interactions. Furthermore, an

ACCEPTED MANUSCRIPT

average loss below 4.1% was recorded after eight cycles, signifying that GO-Fe3O4@P is stable and reusable. Recently, Pan *et al.*, [19] developed GO-encapsulated core-shell magnetic microspheres (GOE-CS-MM) using a self-assemble approach between negative charged GO sheets and positive charged poly(diallyldimethylammonium) chloride (PDDA)-modified Fe_3O_4@SiO_2 via electrostatic interaction. The adsorbent is efficient for the extraction and cleanup of environmental phenol from seafood samples and could also lessen matrix effect following hydrogen bonding between impurities in the extracts and, and π-π stacking interaction process. This shows that GOE-CS-MM is an excellent cleanup adsorbent for complex matrix samples.

2.1.3. Moleculary Imprinted core–shell NMPs

The need for a higher adsorption capacity as well as selectivity has made some researcher opt for alternative adsorbent such as molecularly imprinted polymer [59], which is prominently used for production of tailor-made recognition materials with cavities that favors selectivity of specific molecules[20, 60]. MIPs have been extensively utilized for sensor devices [61], protein separation [62], and solid-phase extraction [63, 64]. Nevertheless, MIP prepared via the conventional technique exhibit some shortcomings such as heterogeneous distribution of the binding sites, poor site accessibility for template molecule, embedding of most binding sites and complexity of the preparation procedure. Suspension polymerization is mainly suitable for porous imprinted polymer nanoparticles synthesis, but limited by its propensity to generate a wide range of particle sizes from micrometers to millimeters, as well as the dispersing medium negative infuences [15]. Imprinting by grafing on the surface of silica nanoparticles or organic polymeric is capable of generation the desired polymer morphology, but it exhibits low extraction capacities [15]. Ultrasound technology (e.g. ultrasoundinduced hydroalcoholic emulsion) is a feasible alternative towards obtaining a better conversion and polymerization reaction rates as well as energy saving

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[65-67]. Furthermore, the formation pathway as well as the physical properties of the polymers generated from this technique are less affected by ultrasound [66].

Finally, the complexity associated with the preparation procedure could be alleviated by combining grafting reaction with ultrasound-assisted suspension polymerization [15]. This hybrid technique will synergistically combine the remarkabbe morphology formation grafting method with the outstanding reaction rates and conversion as well as energy saving capability of ultrasound assistance to improve suspension polymerization technique. Zhao *et al.*, [15] developed a novel core–shell nanoring amino-functionalized magnetic MIP (CS-NR-MagMIP) by coupling grafting reaction with ultrasound-assisted suspension polymerization (Scheme 4). They used bisphenol A (BPA) as the template and adsorbate, GMA, MMA and DVB as the monomer, and DVB was used as a cross-linkers. Their reported revealed that the CS-NR-MagMIP gives higher adsorption capacity (750.2 mg/g), faster binding ability, and better selectivity than the CS-NS-Mag-MIP (275.0 mg/g) synthesized by conventional mechanical agitation (CMA), and amino-functionalized nonimprinted NMP (CS-NR-Mag-NIP) (125.0 mg/g). The ultrasound assistance during suspension polymerization reduces the formation of secondary nucleation and the period of nucleation, facilitating the binding of more amino groups to the surface of the magnetic cores by the grafting reaction [15, 68].

Furthermore, the challenges facing MIP technique can also be solved by using graphene oxide (GO) to act as MIP solid-support substrate. This becomes a viable technique because GO exhibits large delocalized π-electron system, remarkable mechanical property, and high specific surface area [69]. MIP modified GO could also a better mass transfer and lower permanent entrapment of the template. Pan *et al.*, [20] employed reflux-precipitation polymerization and surface imprinting

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

method for rational design of magnetic GO sheet embedded with core–shell MIP microspheres (MGO@MIP) for removal of pentachlorophenol (PCP) from environmental water. They reported that the adsorbent exhibit a remarkable performance based on adsorption capacity and specific selectivity. The q_m and the imprinting factor (α) obtained are 789.4 mg/g and 4.36, respectively at 4.0 pH and a monomers/Fe3O4 ratio of 15. Furthermore, an average loss below 5.6% was recorded after ten cycles, signifying that MGO@MIP is stable and reusable.

The remarkable performance can be ascribed to the synergetic effect of π–π interactions and hydrogen bonding, which are extremely related with the pH of the solution, and magnetic microspheres distribution on GO sheets surface.

Pan *et al.*, [69] also developed a novel double-sided magnetic MIP modified GO (DS-MMIP@GO) adsorbent. The preparation procedures follow solvothermal reaction, precipitation polymerization, and surface-imprinting technique. They used the adsorbent to develop a MSPE procedure, which was coupled with LC–MS/MS to effectively enrich and swiftly detect trace-level microcystins (MC) from a large volume of water. This developed MSPE-LC–MS/MS procedure exhibits larger enrichment factor (2000) and considerably lower LODs (0.03–0.61ng L^{-1}) when compared with the earlier reported methods [70, 71]. In a recent study, Pan *et al.*, [53] developed an *in situ* controllable technique towards fabricating a well-designed GO-based ternary magnetic MIP polymer hybrid (T-MMIP hybrid). This was achieved by modifying the GO sheet with Fe_3O_4 microspheres using a one-pot solvothermal technique to produce GO-Fe_3O_4 prior to *in situ* co-polymerization and subsequent template molecule elution. They used acrylamide (AM), DVB, and microcystin-LR (MC-LR) as monomer, cross-linking agent and template molecule, respectively. Under the optimum conditions (template molecule to functional monomer to cross-linker molar ratio of 1 : 4 : 10), the T-MMIP hybrid demonstrated a remarkable affinity towards eight MCs

ACCEPTED MANUSCRIPT

similar structure (MC-WR, MC-YR, MC-LF, MC-LA, MC-LY, MC-LW, MC-LR, and MC-RR) in aqueous solution. The enrichment factors of T-MMIP hybrid for the eight MCs reported to be greater than 2000. This shows that the binding of T-MMIP hybrid with the original template MC-LR at optimum condition had significantly improved the selectivity and affinity for a group of structurally related MCs when compared with the literature [53, 72]. The adsorption proceeds by the synergistic effect of hydrogen bonding (between MC molecules and amine groups on the microspheres), and π-π stacking interactions (between the double bonds and benzene ring on GO sheet and MCs) [53].

[Insert Table 1]

4. Polyssacharides

Polysaccharides are ultra-lightweight, abundant, inexpensive, renewable, typically biodegradable and biocompatible compounds mainly used in the field of sustainable chemistry. They are capable of associating by chemical and physical interactions with numerous molecules. Polysaccharides such as starch, and their derivatives (cyclodextrin, chitosan, and chitin) [73]. Kumar [74] have gained imense attention towards developing a more effective and inexpensive adsorbent unlike synthetic ionexchange resins and AC. The choice of these biopolymers as smart alternative adsorbents is due to their chemical stability, particular structure, high reactivity, physico-chemical characteristics, and remarkable selectivity towards metals and aromatic compounds. This is attributed to the presence of chemical reactive groups (amino functions, acetamido or hydroxyl) in the polymer chains. The presence of repetitive functional groups in biopolymers makes them excellent complexing and chelating materials for numerous contaminants such as aromatic

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

compounds, heavy metals and dyes [73]. Despite the fact that polysaccharides and their derivatives naturally exhibit remarkable sorption property, their adsorption capacity can be selectively enhanced by the substitution of various functional groups onto the backbone of the polymer [73]. Polysaccharides can be regenerated by desorption at a cost effective rate if necessary. It is easy to regenerate them by using washing solvent because the interaction between the adsorbent and the pollutant is mainly driven by hydrophobic, electrostatic and ion-exchange interactions [73]. Therefore polysaccharide derivatives can be used as a cheap adsorbent of choice in water treatment for removal and separation of contaminants, and a useful environmental protection tool [75]. However, scaling up for commercialization is a difficult task adsorption properties of polysaccharide derivatives such as chitosan and chitin depend on the sources of the polysaccharide, the molecular weight and solution properties and varies with crystallinity, degree of N-acetylation, percent deacetylation [76], affinity for water, and the content of amino group [73]. These parameters are determined by the operating conditions used during the preparation [75], and they control the diffusion and swelling properties of the polysaccharide and its characteristics. Furthermore, cyclodextrin exhibits a distinct geometry, and the inclusion process is influenced by polarity, size and shape of contaminants, as well as the size of the CD cavity. The adsorption efficiency of polysaccharides depends on physicochemical properties such as particle size, surface specific area and porosity of sorbents. However, polysaccharide derivatives have poor porosity and low surface area. Further disadvantages are the fact that they are denaturalized by extreme temperature and pH variation, and their application in packed columns was restricted by morphological and physical properties. Furtunately, these mentioned disadvantages can be overcomed by reinforcing and/or supporting them.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

4.1. Chitosan

Chitosan is a renewable cationic biopolymer (β-[1 → 4]-2-amino-2-deoxy-D-glucopyranose) obtained by partial or total deacetylation of chitin (a biopolymer) (Figure 3), which is mainly sourced from aquatic species, and is the most abundant natural polysaccharide after cellulose [75]. Chitosan could be used as a coagulant-flocculant since it is capable of coagulating various ionic substances like dyes and metal ions, making it suitable for sustainable treatment of wastewater [77]. It is characterized by its crystallinity, degree of deacetylation (DD) or degree of acetylation (AD), and molecular weight [78]. These features depends solely depends on the preparation method. For instance:

- Chemical degradation is more suitable for large scale synthesis of low molecular weight (LMW) chitosans with Mw 5–15 kDa.
- enzymatic hydrolysis is more appropriate for preparation of chitosan oligomers with low polymerization degree (2–10).
- depolymerization of water soluble chitosan (WSC) using cellulase at optimum condition of pH 4.5 and 60°C will effectively produce LMW WSC with broad molecular weight (600–1.5 kDa).

[Insert Figure 3]

Chitosan production entails a chemical deacetylation process. Commercial production of chitosan by deacetylation of crustacean chitin with strong alkali seems to have inadequate potential for industrial acceptance particularly due to the difficulties in handling the large amount of concentrated alkaline waste generated, leading to environmental pollution. However, chitosan and chitin could also be found in the septa and cell wall of yeasts and filamentous fungi. They are

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

readily cultured in simple nutrients and used to produce chitosan. Chitosan preparation from fungal cell walls using the current fermentation technology in an ecofriendly manner.

Biosorption on chitosan is an emerging treatment technology that overcomes the selectivity limitation of adsorption processes (especially with AC). Chitosan beads exhibit superior selectivity as compared with traditional resins and can reduce contaminant concentrations to ppb range unlike AC that is limited to ppm levels [73]. Its remarkable features include high binding capacity for metal ions, low cost, nontoxity and recyclability, making it a suitable alternative for conventional synthetic polyelectrolytes [75]. Table 2 presents the multiple physicochemical properties of chitosan and its polyelectrolytic properties at acid pH.

[Insert Table 2]

Several authors have studied chitosan affinity for transition metal ions [79, 80]. The study of Krajewska [79] revealed that the affinity of transition metal for chitosan membrane are in coefficient order of $Cu^{2+} < Ni^{2+} < Zn^{2+} < Mn^{2+} < Pb^{2+} < Co^{2+} < Cd^{2+} < Ag^{+}$. This corresponds to the sequence of the affinity of metal ion-polymer, which confirms the chelation of the ions by chitosan. Kaminski [80] tested chitosan beads with Cr^{2+}, Cu^{2+}, Zn^{2+} and revealed that the adsorption sequence is in the order of $Cu^{2+} > Zn^{2+} > Cr^{2+}$. This shows that chitosan has a stronger selectivity for Cu^{2+}, however, the adsorption sequence changed to $Zn^{2+} > Cu^{2+} > Cr^{2+}$ at high metal ion concentration.

Chitosan-based materials possess low affinity for basic dyes but high affinities for heavy metal ions, making chitosan chelation a choiced procedure for extraction and concentration methods during heavy metals removal. Chitosan possess extremely low specific area, which range between 2 and 30 m^2g^{-1}, glutaraldehyde crosslinked chitosan beads [81] has 60 m2g-1, whereas most commercial ACs exhibit a specific area ranging from 800 to 1500 m^2/g. Mi *et al.*, [82] developed

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

a new technique for the synthesis of porous chitosan beads by using a wet phase-inversion technique. Delval *et al.*, [83] developed porous crosslinked starch by formation of gas bubbles within the material during the synthesis. The particle size of adsorbents also a vital parameter that influences the sorption performances [83]. Generally, the random variation of adsorption capacity is because of the particle size variation [83]. The removal rate increases with a decrease in the particle size due to increase in the effective surface area, while the time needed to attain the equilibrium increases significantly with the particle size of the adsorbent [84]. Furthermore, the adsorption performance also depends on several factors such as the adsorbent properties like crystallinity, the degree of crosslinking and rigidity of the polymeric chains, and the chemistry of the contaminant.

To boost the suitability of chitosan for industrial application, it could be reinforced/supported by organic or inorganic matrixes which are synthetic in nature such as minerals and polymers, or it may be self-croslinked by adding suitable chemicals [84].

Chitosan can be reinforced by mixing with a crosslinker, which must have at least two reactive functional groups capable of transforming the chitosan chemically by creating bridges between its polymeric chains or adjoining molecules. The crosslinker matrix should allow the flow of the pollutants towards the particles of the supported chitosan and simulteinously ensuring the physical and chemical stability of the chitosan [84]. Prominent among the crosslinkers used for reinforcement of chitosan are glutaraldehyde [18], tripolyphosphate, silicate, polyvinyl alcohol, glyoxal thiourea and cellulose.

However, it is important to know that modification of chitosan with reinforcement or supporting matrix lowers its adsorption capacity and the intraparticle diffusion irrespective of the support/reinforce employed. Meanwhile, to ensure the adsorption capacity close to that of the

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

parent chitosan, additive such as Fe_3O_4, alginate [85], polyethylenimine, chloroacetic acid (HClAc) and Fe is necessary. A suitable additive should be chemically or physically affine to chitosan and also have chemical groups that can remove the targeted pollutant, or at least remain inert toward the biosorbent [84].

Marrakchi *et al.*, [86] reinforced chitosan with epichlorohydrin [87] as the crosslinker and sepiolite clay as an aditive to produce a crosslinked composite material for removal of reactive orange 16 (RO 16) and methylene blue (MB) from aqueous solution. They reported that the maximum monolayer adsorption capacity of composite (using chitosan to sepiolite weight ratio of 1, Initial dye concentration of 100 mg/L and adsorbent dosage = 1 g/L at 30 °C for 30 h) for RO 16 and MB are 190.97 mg/g and 40.99 mg/g, respectively. The adsorption process was best described by Freundlich model, and pseudo-second-order kinetics gives a better description of the process for both dyes. This performance is by far better than most of the previous work reported by [88] (11.94 mg/g), [89] (10.91 mg/g), [90] (24.690 mg/g), and [91] (37.04 mg/g) for MB. Sami *et al.*, [77] also reported a remarkable performance for crosslinked chitosan (using glutaraldehyde as a crosslinker and starch as an additive) for removal of Congo red dye (a toxic anionic dye) from wastewater by flocculation.

Chitosan can be reinforced by insertion of compounds such as vinyl monomers into the its original chemical structure by grafting. This involves dissolution of chitosan in the compound, which makes the chitosan to lose its unique properties, thereby decreasing its chemical and mechanical resistance [84]. The fact that chitosan and crosslinked chitosan have low affinity for cationic (basic) dyes has necessitated the search for an alternative modification technique fo chitosan. Grafting is an effective technique for chitosan modification towards increasing its molecular weight as well as its water-solubility towards enhancing the adsorption performance and selectivity

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

for both cationic and anionic dyes. This provides a suitable environment for hydroxyl groups and abundant amino groups in the chitosan backbone to interact with vinyl monomers under mild conditions. Establisment of a flexible grafting chain enhances the migration of the flocculant to the particles in wastewater, thereby improving the flocculability. Wang *et al.*, [92] prepared a highly water-solubile chitosan based flocculant by grafting it with (2-methacryloyloxyethyl) trimethyl ammonium chloride (DMC). By optimizing the reaction parameters they were able to achieve grafting percentage above 236.4%. The synthesized flocculant exhibits a more remarkable flocculation capacity and efficiency than that of polyacrylamide.

Although crosslinked chitosan has overcomed the challenges of poor heat resistance and unsatisfactory mechanical properties as well as soluble in acidic media associated with the use of chitosan, its performance in packed column is yet poor. Crosslinked beads crumbles easily and exhibit lower swelling percentage [93]. Therefore, it does not function ideally in packed-column configurations, which is usual of pump-and-treat adsorption practices. Several authors have established that rationally designed chitosan-based composites are capable of overcoming these problems [93]. Chang & Chen [93] designed a chitosan-conjugated magnetic nano-adsorbent for removal of anionic dyes from textile wastewater. They reported a remarkable adsorption capacities 1471 and 1883 mg of dye/g of chitosan for AG 25and AO 12. Chen et al., [94] developed α-cyclodextrin (CD)-linked chitosan bead for removal of six different phthalate esters from aqueous solution in a column setup. They reported an excellent removal efficiency (3.21 mg/g) for diheptyl phthalate (DHpP). Upon regeneration in a mixture of methanol and water and about 94.6% of the adsorbed DHpP was recovered, and the adsorbent was reused 20 times in a batch test.

ACCEPTED MANUSCRIPT

4.2. Cyclodextrin

Cyclodextrins (CDs) are cyclic oligosaccharides, which comprise of 6 (α), 7 (β), 8 (γ) glucopyranose units interconnected via α (1–4) linkages [95] obtained by degrading starch enzymatically with bacteria [96]. They form a ring structure in form of torus, containing an apolar cavity with primary hydroxyl groups, which lie on the outside and secondary hydroxyl groups inside. They exhibit amphiphilic character, which makes them so attractive as adsorbents because they are so hydrophilic that they significantly swell in water, thereby enabling fast diffusion of adsorbates, while they simultaneously have extremely hydrophobic sites, which proficiently extract non-polar contaminants [73]. CD based adsorbents have low affinity for metals but an outstanding capacity to form inclusion complexes with organic molecules, particularly the aromatics. Therefore, the nature of the contaminant is a major determinant of the choice of adsorbent. However, native CDs are water soluble, making the unsuitable for direct for removal of organic contaminants from water [95].

The solubility issue associated with CD can be overcomed by crosslinking the CD with crosslinkers such as isophorone diisocyanate, toluene-2,6-diisocyanate, hexamethylene diisocyanate, EPI etc. to form insoluble β-CD based polymers. β-CD based polymers have ability to effectively remove inorganic contaminants like heavy metal, organic contaminants and dye from wastewater [97]. Prominent of all the crosslinker employed in polysaccharide chemistry is EPI especially bifunctional EPI, which has two reactive functional groups: An epoxide group and a chloroalkyl moiety that is capable of reacting with the OH groups of CDs under alkaline condition (Fig 4) [98]. The product of this interaction is a heterogeneous mixture of different CD glyceryl ethers [99].

[Insert Figure 4]

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Salipira *et al.*, [100] prepared β-CD-EPI nanospheres for removal of very low concentration *p*-nitrophenol (*p*-NP) from wastewater. The value of q_m obtained was 17.203 mg p-NP per gram of β-CD nanospheres at β-CD/EPI=1/55 mole ratio. They reported that the adsorption of p-NP onto β-CD-EPI nanospheres was efficiently described by Langmuir model. The adsorption efficiency is mostly influenced by β-CD/EPI mole ratio, base concentration and reaction temperature. Organic contaminants such as chlorophenols (CPs), volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and alkylphenols. Charles *et al.*, [101] prepared β-CD crosslinked with 1,4-butanediol diglycidyl ether in the presence of 2,3-epoxypropyltrimethylammonium chloride, NH_4OH and chloroacetic acid solution (for carboxymethylation). The produced polymeric adsorbent was used for combined lab-scale treatment of polycontaminated industrial effluents containing a mixture of organic pollutants (CPs, VOCs, PAHs, APs) in an oriented-sorption process. The treatment, which paired advanced oxidation with sortption on a β-CD based material showed a remarkable performance by completely eliminating organics such as nonylphenol, 1,2-dichlorobenzene, chloroform, phenanthrene and 2,4,6-trichlorophenol, which are tough to eliminate from complex mixtures when present as traces. The COD and TOC were reported to be lowered by over 93% and 84%, respectively.

Crini [102] also used EPI as the crosslinking agent to recticulate CD in the presence of carboxymethylcellulose (CMC). The resulting adsorbent was used for removal of three basic dyes (C.I. Basic Violet 10 (BV 10), C.I. Basic Violet 3 (BV 3) and C.I. Basic Blue 3 (BB 3)). The adsorption process proceed by spontaneous chemisorption for all the dyes with q_m of 35.8, 42.4 and 53.2 mg of dye per gram of adsorbent for BV 3, BB 3, and BV 10, respectively. The variances in the value of q_m is attributable to the difference in the structure of dye.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Crosslinked CDs fortified with carboxylic groups are efficient for removal of organic matters and metals in a competitive environment where these contaminants compete with other contaminants for the adsorption sites of the adsorbent. the adsorption process proceeds by inclusion complexes for removal of organic matters, while metal removal is by precipitation, electrostatic interactions and ion exchange [103]. Euvrard *et al.*, [103] showed this by developing a crosslinked β-CD using hydroxypropyl (HP) as the crosslinker in the presence of 1,2,3,4-butanetetracarboxylic acid (BTCA). The adsorbent was applied to remove contaminants from spiked solutions and discharge waters from the surface treatment industry. The spiked solutions contain five three alkylphenols (AP), sixteen polycyclic aromatic hydrocarbons (PAH) and metals. The adsorbent exhibited remarkable adsorption capacities: 69 to 90% of the APs, 65 to 82% of the PAHs, as well as >99% of Co^{2+}, Ni^{2+} and Zn^{2+} were removed. The high concentrations of calcium in the industrial discharge waters constitutes competition effects competing with other contaminants for the adsorption sites of the polymeric material.

Magnetic adsorbents exhibit relatively high surface area and are easy to manipulate and separate in complex multiphase systems due to their external magnetic field [95]. Magnetic adsorbents can be synegistically combined with CD by grafting to form a CD based magnetic nanocomposites (Fig. 5). This becomes necessary since CD exhibits low surface area and hard to separate from aqueous phase. CD based magnetic nanocomposites combine the superparamagnetic properties and high surface area to volume ratio of the magnetic nanoparticles with the complex formation between the contaminants and β-CD [104]. These nanocomposites are targeted towards removal of toxic metals from aqueous solution without diffusion resistance. Badruddoza *et al.*, [95] also used carboxymethylated (CM) β-CD based magnetic nanocomposites for competitive and non-competitive removal of Ni^{2+}, Cd^{2+} and Pb^{2+} ions from wastewater. In non-competitive removal,

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

they reported that the values of qm are 13.2, 27.7 and 64.5mg g−1 for Ni^{2+}, Cd^{2+} and Pb^{2+} ions, respectively in 45 min at 25 °C. In competitive adsorption experiments, The adsorbent preferentially adsorb Pb^{2+} ions with an affinity order of $Pb^{2+} >> Cd^{2+} > Ni^{2+}$, which is in agreement with hard and soft acids and bases (HASB) theory [95]. The presence of carboxymethylated in the nanocomposite boosts the complexing abilities of the adsorbent. The removal process is influenced by temperature, ionic strength, and pH. The adsorbent also demonstrate remarkable reusability.

[Insert Figure 5]

β-CD based magnetic nanocomposites can also be used for removal of azo dyes from textile wastewater [105]. This is because β-CD based magnetic nanocomposites is highly hydrophilic derivative of β-CD with additional hydroxyl groups, lower toxicity and better water solubility when compared with β-CD. They also have high ability to form complexes and high capacity for solubilization of organics, and are environmentally benign [106]. Yu *et al.*, [96] functionalized Hydroxypropyl-β-cyclodextrin (HP-β-CD) with Polyethylene glycol 400 (PEG400) prior to grafting on Fe_3O_4 nanoparticles. The presence of PEG400 in the nanocomposite helps to improve its the aqueous solubility. The nanocomposite was efficient for removal of congo red (CR), a typical anionic azo dye from aqueous solutions. The value of qm is 1.895 g/g, which is about 19 times higher than that of Fe_3O_4 nanoparticles. The nanocomposite is a promising adsorbent for removal of CR from textile wastewater, and it exhibits a remarkable reusability.

5. Covalent organic polymers

Covalent organic polymers (COPs) are networks of porous organic molecules interlinked by covalent bonds between monomers [107]. They are recently discovered as new, universal, and functionalized adsorbents because of their low cost, and reusability [108], robust properties [109], significant selectivity among gas molecules [110], which make them a promising adsorbent for

ACCEPTED MANUSCRIPT

wastewater treatment especially for heavy metal. Furthermore, COPs are extremely stable in various harsh conditions like high temperatures even in boiling water [21]. They have been efficiently applied for environmental applications, such as groundwater remediation [22], solvent uptake [23], and carbon dioxide capture [109, 111]. Ko *et al.*, [107] developed disulfide linked polymer networks (COP-63) and engaged as an adsorbent for removal of heavy metal ions from stormwater. They reported that COP-63 shows Cd^{2+} removal efficiency equivalent to that of extremely porous AC despite its moderate surface area. On the other hand, the adsorption kinetics of COP-63 is 16 times faster than that of AC (Fig. 6) [112]. The remarkable performance is ascribed to the high affinity of Cd^{2+} towards thiol and disulfide functionality in the polymer network. From the pH effect and kinetic studies, it is vivid that the adsorption mechanism is chemisorption, indicating the binding of heavy metal on thiol and disulfide sites of the polymer networks. COP-63 is also efficient for Cu^{2+}, Zn^{2+}, and Cd^{2+} due to their high binding affinity in the polymer network, even with competing cations such as abundant earth metals, and Ca^{2+} in the solution. The fast adsorption kinetic for removal of heavy water demonstrated by COP-63 makes it a suitable candidate for treatment of large volume of stormwater runoff where peak flows shorten the residence times [112].

[Insert Figure 6]

Despite the success of COP in heavy metals removal, more works need to be done towards its full-blown applications for environmental remediation. Columns fabricated with such particles size are not viable for typical remediation process due to generation of very high back pressures similar to what is obtainable in high performance liquid chromatography (HPLC) columns [17]. Consequently, the process will require a very high energy to overcome the back pressure for large-scale operation. Moreover, generation of millimeter-scale particles by polymerization of the

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

solidified gel-like polymers will culminate in low treatment efficacy due to inadequate contact time of the contaminant with the column material and slow intra-polymeric diffusion [17, 23]. Therefore, to ensure economic viability in environmental remediation, rational design of column containing extremely functional porous materials (particle size in millimeters) is required for efficient treatment of large volumes of contaminated stream of water. COPs exhibit nano- to micrometer scale [21, 22], as well as macroscale solidified gel-like materials [23].

This could be achieved by supporting COPs on an inexpensive backbone material, thereby providing an ideal solution for developing an economically viable purification process [17]. One of such backbone is nano-sized zero valent iron (nZVI). nZVI exhibits large surface areas and remarkable reductive properties, making it suitable for the degradation of contaminants such as halogenated organic compounds and azo dyes [113]. Mines *et al*., [114] developed composites of nZVI impregnated within various COPs (water miscible (COP-1, COP-19), and immiscible (COP-6, COP-60 and COP-61) for decolorazation of azo dye. The composite materials produced by water miscible COPs exhibit remarkable decolorization efficiency (96% and 95% in COP-19 and COP-1, respectively for 30 min), while the immiscible shows very poor performance (Fig. 7). The decoloration efficiency is determined by BET surface area, as well as distinct properties of the linker/core molecular composition of each COP, especially their wettability in contaminated solution. The decoloration rate of the COPnZVI-composite using miscible COPs are similar to that of pure nZVI alone when used for azo dye decolorization [114]. The decolorization mechanism of COPnZVI-composite was studied by conducting a parallel control experiment with COPs and nZVI and it reveals a synergistic effect of adsorption onto COPs and degradation by nZVI. COPnZVI-composite could also be effectively used for treatment of several groundwater

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

contaminants like halogenated organics (e.g. TCE) because they exhibit a similar chemical reduction mechanism.

[Insert Figure 7]

Another viable backbone is granular AC (GAC). Combining GAC with COPs will coverup the lack of selectivity exhibited by of AC treatment process. GAC is capable of providing optimum backbone for COPs attachment due to its compatible chemistry for polymers grafting to its surface and the suitability of its particle size for fabrication of packed-bed column with low energy demand [17, 115]. Mines *et al.*, [17] developed COP-19 functionalized GAC (AC-COP) by functionalizing the GAC surface with COP-19 prior to the creation of a COP ‘‘shell” all over the carbon granule (Fig. 8). The synthesized AC-COP display a core-shell form of COP material grafted to the GAC outer layers. AC-COP adsorbent demonstrated a remarkable removal efficiency for heavy metals(Cd^{2+} and Fe^{3+}) and organic dyes (azo dye). Comparatively, adsorption with COP-19 and GAC were also studied. AC-COP and COP-19 demonstrated a high affinity for removal of azo dye barely after 30 min. This performance is similar to the previous report of [22] using COP-19. The adsorption capacity of AC-COP and COP-19 and GAC are 23.6, 23.8, and 5.6 mg/g, respectively This shows that AC-COP is a promising adsorbent for environmaental application due to its cost effectiveness, roburstness, versatility and durability.

[Insert Figure 8]

6. Extracellular polymeric substances (EPS)

EPS are complex extracellular polymers formed by microbial aggregates. They possess high molecular weight and comprise of mixture of macromolecules such as polysaccharides, proteins, uronic acids, lipids, DNA, and humic-like substances [116], which envelope the microbial cells in a three-dimensional matrix. EPS play vital roles in common biological wastewater treatments such

ACCEPTED MANUSCRIPT

as membrane bioreactors (MBRs), activated sludge processes and fixed-film processes. It significantly affects the dewaterability floc size and stability, settleability and flocculability for flocs and sludge retention and biofilms shear resistance [24, 25]. EPS are categorized into two major fractions: soluble EPS (SEPS) (soluble colloids, slimes, and macromolecules) and bound EPS (attached organic materials, loosely bound polymers, sheaths, condensed gels, and capsular polymers) [117]. Soluble EPS are also known as soluble microbial products (SMP), which absolutely dissolve into entire solution or form a weak bound with cells, while bound EPS discretely cover the layer with separate margin outside the entire cell walls [117]. Generally, the category of EPS recorgnized in literature and in this article are bound EPS. Bound EPS are characterized with a dynamic double-layer-like structure [118] (Fig. 9), and are categorized as loosely bound EPS (LB-EPS) [119], which diffuses by extraction technique in the outer layer, and tightly bound EPS (TB-EPS), which constitutes the inner layer. The variation of EPS fraction solely depends on the microbial aggregate types. For instance, the zeta potentials of different EPS are in the descending order of LB-EPS > TB-EPS > SEPS for S-sludge and TB-EPS > LB-EPS > SEPS for biofilm. The flocculating capacity of each EPS fraction was SEPS < LB-EPS < TB-EPS, and the EPS fraction in the biofilm is lower than that of the corresponding EPS fraction in the S-sludge [120]. This shows that the role of EPS in S-sludge is more significant in microbial cell aggregating when compared with those of biofilm.

[Insert Figure 9]

The physico-chemical characteristics and composition of EPS exhibit significant impact on the maintenance of the process performance and bioaggregate structure in treatment of wastewater

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[121]. The composition of EPS have high molecular weights from charged functional groups that exhibit both adhesive and adsorptive properties. Ideally, EPS function as a natural ligand source that provides binding sites for other charged particles or molecules as well as metals due to the availability of charged moieties [121]. They have capacity to prevent or delay toxicants from interacting with microbial cells by chemical reactions and/or mass transfer limitation. This enable adsorption of heavy metal ions by EPS, preventing them from entering the cells, thereby reducing the potential toxicity of heavy metal to the bacteria functioning in the activated sludge. EPS also help to adsorb phosphorus in biological P removal (BPR) systems [14, 122] due to the adsorption of PO_4^{3-} (charged ion) to the minerals with positive charge (like Al and Fe oxides) in EPS. Consequently, the role of EPS in P removal EBPR systems enriched with heavy metal is so crucial. So, it is necessary to investigate the variation of heavy metals in the composition of EPS in sludge containing phosphate-accumulating organisms (PAOs) or the role of EPS when exposed to long-term stress from heavy metals. The study of Wang *et al.*, [121] revealed the role of EPS in the company of heavy metals in BPR systems towards developing a stable denitrifying P removal (DPR). They did this by varying the amount of Cu(II) from 0 to 3 mg/L in a sludge containing PAOs. They reported a remarkably high P removal efficiency even as the amount of Cu(II) was increased up to 2.5 mg/L, but the efficiency declined when the amount of Cu(II) was increased to 3 mg/L. The content of EPS, comprising humic substances and proteins increases as the amount of Cu(II) increases towards 2.5 mg/L. This property of EPS helps to protect PAOs against heavy metals because both humic substances and proteins are strong ligands for Cu(II) [123]. The aromatic proteins were converted to soluble microbial byproduct-like material when the PAOs were exposed to Cu(II) stress, due to the complexing capacity of the strong metal ion. There was an enhancement in the detoxification performance of the sludge EPS when the percentage of humic

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

substances increases. EPS binds the heavy metals toxicity and P storage, thereby protecting the microbes againt heavy metals to enhance the stability of DPR systems.

Several authors have also reported that EPS possess a number of reducing functional groups that are capable of heavy metal reduction. Kang & Zhu [124] suggested that the EPS reduction capacity is attributed to the presence of hemiacetal reducing ends in phenol groups and polysaccharides. Nevertheless, because EPS have a weak reduction capacity, heavy metals reduction by EPS devoid of cells is exceptionally slow, thereby showing insignificant effect on heavy metals species. However, Zhang *et al.*, [125] developed a strategy towards accelerating the reduction of heavy metals. They utilized EPS from Shewanella oneidensis MR-1 under illumination for reduction of silver ions (Ag^+) to form silver nanoparticles (AgNPs) [64]. Illumination via UV irradiation helps to accelerate the reduction process. The illumination stimulates AgNPs for their surface plasma resonance (SPR) by accelerating the electrons from the EPS towards Ag^+ (Fig. 10). The illumination could also stimulate the EPS molecules to form a strong reducing species, which mediates the reduction of Ag^+. This is predicated on the fact that natural sunlight influences the redox of some metal ions like Ag(I), Cr(VI), Hg(II), Fe [126] in an aqueous solution containing humic substances due to formation of several redox-active species under irradiation of light [127].

[Insert Figure 10]

Despite the fact that EPS have a positive impact on the properties and roles of bioaggregates in wastewater biotreatment systems, and they also contribute to formation and stability of biofilm, sludge behaviors including granulation of sequencing batch reactors (SBRs), they also cause fouling of membrane in membrane bioreactors (MBRs) [117].

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

6.1. EPS in Fixed-film

EPS matrix is the largest component of biofilm (>90%), the remaining part compose of microorganisms, which are < 10% on the dry basis [128]. EPS matrix engender formation of stable biofilm, facilitate their adhesion to surfaces and subsequently cultivate a three-dimensional cohesive architecture towards interconnecting and transient immobilization of biofilm cells [129]. This process is known as fixed-film process. The biofilm is produced on an inert support medium with a big specific surface area to maximize biofilm formation, thereby removing colloidal and dissolved organic contaminants [130, 131]. Moreover, the role of EPS matrix in biofilm also include recycling, which entails preservation of all the components of the available lysed cells [129, 132]. Therefore, EPS is a major determinant of biofilm properties, which automatically affect the fixed-film processes performance.

6.2. EPS in Activated sludge

Activated sludge process entails oxidation of microorganisms, biological coagulation, and adsorption in the sludge to remove the coagulated organic matters. The properties of sludge are crucial to general performance, treatment efficiency and emission quality. EPS constitutes about 80% of the entire activated sludge mass [117]. In conventional activated sludge processes, The presence of EPS in the sludge cultivates the sludge structure, facilitates cell-to-cell interactions and sludge stability. The sludge stability increases with increase in the content of EPS in the sludge [24]. Increase in the composition of protein in the EPS increases the hydrophobicity of the sludge, which culminates in enhanced flocculation. However, excess EPS in activated sludge could reduce the settleability of the sludge. Moreover, EPS also plays a vital role in the sludge dewatering capability whereas excess EPS generally declines sludge dewatering ability [117]. The presence

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

of EPS is crucial in formation, structural and functional reliability of aerobic granule sludge in SBRs processes. EPS mediates granulation of sludge, and binding of cells via polymer entanglement, hydrophobic interaction and ion bridging interaction, thereby enhancing and promoting granules formation [24]. Therefore, EPS plays a vital role in determining the properties of activated sludge, thereby influencing sludge performance.

The study of Xu *et al.*, [133] shows that the hydrophobic interaction established by EPS in activated sludge can generate driving force that will enable a spontaneous interaction between sulfamethazine (a typical antibiotic) and the proteins in EPS. This shows the relevance of EPS in removal of antibiotics from activated sludge system.

Although EPS promotes settleability, excess amount of EPS declines sludge settleability. On the other hand, recent studies show that the role of EPS on the dewaterability and settleability of activated sludge can be improved by ultrasonic pretreatment [119, 134, 135], and hydroxymethyl phosphonium sulfate (THPS) biocide pretreatment [16]. This is achieved by destruction and reconstruction of EPS, thereby improving the solid-water separation processes Chen *et al.*, [25] reported that pretratment with THPS promotes disintegration and biodegradability of sludge, and subsequent volatile fatty acid (VFA) formation as wel as shortening of fermentation time. Ultrasonic energy collapses sludge flocs, disrupts cell walls and minimizes floc size, thereby promoting the release of the substances (external or internal) in the cells and to the flocs. Moreover, sludge settleability is promoted by ultrasonic pretreatment, and the settling effects varies with the sludge size, treatment time and ultrasonic density [136]. Furthermore, the study of Chen *et al.*, [25] reveals that combination of acidification and ultrasonic pretreatment in the present of a chemical re-flocculant (such as poly aluminium chloride (PAC) and polyacrylamide [137]) can efficiently improve sludge settlability.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Apart from ultrasonic, and THPS pretreatment, other methods that accelerate separation in solid-water system by flocs and cells disruption, and solubilization of EPS components include enzymatic treatments, pH control and Fenton's reagent and Fenton-like process pretreatment [138, 139].

6.3. EPS in Membrane bioreactors (MBRs)

MBR is made up of common bioreactors comprising membrane filtration units for retention of biomass [131]. This technology is known to be a high-quality technology of choice for various wastewater treatments. However, the wider application of this technology is stalled by membrane fouling due to the presence of EPS. Generally, the severity and extent of fouling condition is largely determined by the characteristics and concentrations of EPS , which influences the mophology and surface properties of the sludge mixture liquor. The fouling mechanisms include formation of gel layer and cake layer, osmotic pressure effect, changes of foulants layer and pore clogging. Furthermore, the presence of EPS could direct or indirect ignite the fouling potential of other foulants such as colloids, biopolymer clusters (BPC)x, dissolved organic matters (DOM), and SMP [140]. Therefore, the nature and concentration of EPS largely influence the membrane activity, thus affecting the MBRs performance. Meanwhile, EPS control by manipulating the sub-fractions, compositions and properties of EPS and microbial aggregates is key towards maximizing the performance of microbial aggregates and minimizing membrane fouling in MBRs. On the other hand, Deng [141] developed a sponge modified plastic carrier as a functional media to improve the system performance of integrated moving bed biofilm reactor-membrane bioreactor (MBBR-MBR). They reported that the presence of the sponge in a submerged MBR system can inhibit pore blocking and alleviate the formation cake layer, resulting in an effective minimization of

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

membrane fouling. The addition of this functional media also rid the membrane surface of EPS, BPC and/or SMP.

.

6.4. EPS in solubilization treatment

One of the usual concerns affecting EPS pollutant removal is formation of compact clogging layer, which is the same as that of activated sludge [142]. This often occur in Constructed wetlands (CWs) and it can seriously affect the entire treatment performance and operational lifespan. Several authors have dealth with clogging issue in two different techniques. One of the techniques is preventative approaches such as optimization of operational conditions: better grading of substrate and appropriate planting [143]; strategically organizing supply of water and charging; supplementary pretreatment, especially with anaerobic reactions and contact oxidation or SBR and lagoon. Despite the effort of preventative techniques, clogging still takes place after long operation periods [144]. This shows that preventative techniques could not effectively prevent clogging. The second technique is restorative approaches, which tend to reduce clogging after its occurrence. This approaches could be by applying a resting operation or backwashing the substrate, or by excavation of the clogged media and replacement with a clean media [145]. Although thhese methods are relatively effective, they constitute too much of operational efforts that result in high cost, the methods may lead to substrate destruction. They also consume excessive energy and the whole system may take a long time before returning to normalcy.

Other authors have also attempted to eradicate clogging *in situ*, by using chemical technology, which entails the use of supplementary chemical solvents like, sodium hypochlorite, hydrochloric acid, sodium hydroxide, and hydrogen peroxide [146] to aid digestion of clogging deposits, or by using biotechnology means, which utilizes earthworms to accelerate accumulation and

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

biodegradation. The former is efficient but could result in severe chemical damage to the system. The later is safe but faced with earthworm adaptation problem.

Therefore, it is necessary find a suitable technique that is both effective and safe to eradicate clogging *in situ* by dissolving or dispersing the clogging matters. [147] [148] [147] Du *et al*., [132] attempted to achieve this by using biosurfactant rhamnolipid (RL) facilitated solubilization of clogging deposits *in situ* in a CW plant. This technique significantly improved the dispersion and solubilization of clogging deposits. RL enhances dispersion and dissolution of EPS, thereby enabling the release of enzymes embedded in the EPS to enhance removal of pollutant. This approach seems promising for management of clogging since it is said to be effective and not detrimental to the system but more study is necessary to detect the secular effect of the treatment on the systems.

7. Advantages and limitations of using polymeric adsorbent for industrial application

Adsorbent suitable for industrial application should meet the following requirements:

- Cost effective
- Suitable for removal of diverse (hydrophobic) contaminants
- high adsorption and rate capacity
- High selectivity for various concentrations
- Large surface area
- High durability
- Ease of regeneration if required
- Ability to withstand several wastewater parameters

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

In comparison with conventional adsorbents such as synthetic ion-exchange resins and commercial activated carbons, contaminants adsorption using the above discussed polymeric adsorbents offers several advantages and limitations as highlighted in Table 3.

[Insert Table 3]

8. Economic Analysis

Small cyclodextrins such as α-, β-, and γ -cyclodextrin can be obtained easily cheaply via enzymatic interaction between CGTase and starch, and subsequence precipitation of the individual cyclodextrin using an organic compound, popularly known as a selective complexant. Production of a large quantity of cyclodextrins is achievable at a low-cost via this procedure, leading to their commercial success [148]. About 97% of the CDs obtainable in the market are β-CDs because the cost of production of α- and γ-CDs increases considerably due to the need for purification [149]. The effective degradation speed, recyclability, biocompatibility and low cost make β-cyclodextrin a pretty alternative for bioremediation [150].

Bioactive chitosan is produced using enzymatic hydrolysis, which is so expensive. However, hydrolytic enzymes are reused in a sequential and continuous system rather than a batch setup for a cheaper large-scale production of chitosan [151]. Divakaran and Pillai, [152] investigated flocculation of algae using chitosan and reported that about 50,000 to 500,000 L (depending on concentration algal) of water could be treated with 1 kg chitosan, which cost below two US dollars. Nano-magnetic polymers are highly promising as a safe, efficient and economic absorbent for wastewater treatment. Their application is gaining attention in the removal of heavy metal, where they exhibit the ability to enhance adsorption capacity and rate, as well as selectivity for targeted metal ions. They are cost effective and exhibit inherent magnetic properties, which enable fast and

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

facile solid-liquid separation under an applied magnetic field, without centrifugation or filtration [35].

COPs are cost-effective universal adsorbent. They exhibit 100% reusability even at a warm temperature and high pressure. The adsorption kinetics of COP-63 is 16 times faster than that of AC [112]

Based on the market survey for laboratory grade polymeric adsorbent, the prices are presented in Table 4. The price of the adsorbents varies with manufacturers. Cyclodextrin is the cheapest of all, while COPs are the most expensive. The price of the adsorbents is in the order of COPs > NMP > Chitosan > Cyclodextrin. However, the adsorbents are by far cheaper in bulk, making them considerably cost effective.

[Insert Table 4]

9. Conclusion

This study presents varieties of polymeric adsorbents. Some of them are locally available, economical and effective adsorbents that could replace commercially available AC for the adsorption of various contaminants from wastewater. Definitely, polymeric adsorbents offer several promising benefits for industrial application in the nearest future. The polymeric adsorbent considered include nano-magnetic polymers (NMPs), polysaccharides, extracellular polymeric substances (EPS), and covalent organic polymers (COPs). We have shown this by taking a critical look at the recent progresses in the application of these adsorbents and possible modification for optimum performance.

The success of using NMPs based adsorbent is credited to the fact that the magnetic material has exceptional magnetic properties, which enable fast and facile separation in solid–liquid system

ACCEPTED MANUSCRIPT

without centrifugation or filtration. They are extremely potent for adsorption of metal ions. The best form of NMP is the ‘‘Core–shell’’ structured but it has to be rationally designed to obtained the optimum ratio between magnetic core and shell. This is because insufficient magnetic oxide (the core) is capable of terminating the magnetic response due to disorientation of the surface spin, and insufficient polymer component (the ‘‘shell’’) could result in poor adsorption capacity. NMPs could be modified for enhanced performance by functionalizing it with amino groups, supporting with grapheme oxide, and moleculary imprinting core–shell.

Polysaccharides like chitosan and cyclodextrin are promising biopolymers due to their high reactivity, chemical stability, physico-chemical characteristics, and remarkable selectivity for metals and aromatic compounds. This is attributed to the presence of chemical reactive groups (amino functions, acetamido or hydroxyl) in the polymer chains. The presence of repetitive functional groups in biopolymers makes them excellent complexing and chelating materials for numerous contaminants such as dyes, heavy metals and aromatic compounds. Polysaccharides are modified for enhanced performance by crosslinking, grafting, and formation of composite beads.

COPs are promising inexpensive organic adsorbent due to their stability under harsh condition, which make them exhibit a similar removal efficiency to that of AC for heavy metal adsorption inspite of their moderate surface area. COPs can be modified by supporting with inexpensive backbone materials such as granulated AC, and nano-sized zero valent iron (nZVI) for enhanced adsorption performance.

EPS play vital roles in common biological wastewater treatments such as membrane bioreactors (MBRs), activated sludge processes and fixed-film processes. EPS function as a natural ligand source that provides binding sites for other charged molecules or particles as well as metals due to the availability of charged moieties. It significantly affects the dewaterability floc size and

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

stability, settleability and flocculability for sludge and flocs retention and biofilms shear resistance. Their capacity to prevent or delay toxicants from interacting with microbial cells by chemical reactions and/or mass transfer limitation enables adsorption of heavy metal ions by EPS, preventing them from entering the cells, thereby reducing the potential toxicity of heavy metal to the bacteria functioning in the activated sludge. EPS is also capable of adsorbing phosphorus in biological P removal (BPR) systems due to the adsorption of PO_4^{3-} (charged ion) to the minerals with positive charge (like Al and Fe oxides) in EPS.

Furthermore, more work is required to be done to make these polymeric materials viable for industrial application like the conventional activated carbon. The study on chitosan should be rather focused on how to improve the durability and swelling property of crosslinked chitosan beads in column setup. Researchers need to make concerted effort towards proffering solution to the back pressure limitation in the use of COPs in column setups. Rational design of porous COP particles in millimeter-scale is required to solve this problem. Since NMPs have not been tested in a column setup, this is a prospective future research that will contribute greatly to the knowledge of wastewater treatment. Additionally, more work is needed in the development of composite polymeric materials, for instance, a rational combination of NMP, CD, chitosan and COPs, as well as functionalization with GAC.

Acknowledgement

We gratefully acknowledge the High Impact Research (HIR) grant from the University of Malaya for fully funding this study through Project No. “D000011-16001”. We also appreciate the support of Chemical Engineering Department with RP015-2012D grant.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

References

[1] M. Barakat, *New trends in removing heavy metals from industrial wastewater*. Arabian Journal of Chemistry, 4(2011) 361-377.

[2] A.S. Naje, S. Chelliapan, Z. Zakaria, M.A. Ajeel, P.A. Alaba, *A review of electrocoagulation technology for the treatment of textile wastewater*. Reviews in Chemical Engineering, 33(2017) 263-292.

[3] A. Abbas, A.M. Al-Amer, T. Laoui, M.J. Al-Marri, M.S. Nasser, M. Khraisheh, M.A. Atieh, *Heavy metal removal from aqueous solution by advanced carbon nanotubes: critical review of adsorption applications*. Separation and Purification Technology, 157(2016) 141-161.

[4] X. Qu, P.J. Alvarez, Q. Li, *Applications of nanotechnology in water and wastewater treatment*. Water research, 47(2013) 3931-3946.

[5] H. Ge ,T. Hua, *Synthesis and characterization of poly (maleic acid)-grafted crosslinked chitosan nanomaterial with high uptake and selectivity for Hg (II) sorption*. Carbohydrate polymers, 153(2016) 246-252.

[6] B.V. Mohite, S.H. Koli, C.P. Narkhede, S.N. Patil, S.V. Patil, *Prospective of Microbial Exopolysaccharide for Heavy Metal Exclusion*. Applied Biochemistry and Biotechnology, 183(2017) 582-600.

[7] X. Hao, C. Wang, M.C. Van Loosdrecht, Y. Hu, *Looking beyond struvite for P-recovery*. 2013, ACS Publications.

[8] G. Crini, *Non-conventional low-cost adsorbents for dye removal: a review*. Bioresource technology, 97(2006) 1061-1085.

[9] G.A. Adebisi, Z.Z. Chowdhury, P.A. Alaba, *Equilibrium, kinetic, and thermodynamic studies of lead ion and zinc ion adsorption from aqueous solution onto activated carbon prepared from palm oil mill effluent*. Journal of Cleaner Production, 148(2017) 958-968.

[10] S. Shakoor ,A. Nasar, *Removal of methylene blue dye from artificially contaminated water using citrus limetta peel waste as a very low cost adsorbent*. Journal of the Taiwan Institute of Chemical Engineers, 66(2016) 154-163.

[11] P.A. Alaba, Y.M. Sani, W.M.a.W. Daud, *Kaolinite properties and advances for solid acid and basic catalyst synthesis*. RSC Advances, 5(2015) 101127-101147.

[12] M.E. Olya, A. Pirkarami, M. Mirzaie, *Adsorption of an azo dye in an aqueous solution using hydroxyl-terminated polybutadiene (HTPB)*. Chemosphere, 91(2013) 935-940.

[13] W.-W. Li, H.-L. Zhang, G.-P. Sheng, H.-Q. Yu, *Roles of extracellular polymeric substances in enhanced biological phosphorus removal process*. Water research, 86(2015) 85-95.

[14] H.-L. Zhang, W. Fang, Y.-P. Wang, G.-P. Sheng, R.J. Zeng, W.-W. Li, H.-Q. Yu, *Phosphorus removal in an enhanced biological phosphorus removal process: roles of extracellular polymeric substances*. Environmental science & technology, 47(2013) 11482-11489.

[15] Y.-G. Zhao, X.-H. Chen, S.-D. Pan, H. Zhu, H.-Y. Shen, M.-C. Jin, *Self-assembly of a surface bisphenol A-imprinted core–shell nanoring amino-functionalized superparamagnetic polymer*. Journal of Materials Chemistry A, 1(2013) 11648-11658.

[16] Q.-L. Wu, W.-Q. Guo, X. Bao, R.-L. Yin, X.-C. Feng, H.-S. Zheng, H.-C. Luo, N.-Q. Ren, *Enhancing sludge biodegradability and volatile fatty acid production by tetrakis*

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

hydroxymethyl phosphonium sulfate pretreatment. Bioresource Technology, 239(2017) 518-522.

[17] P.D. Mines, D. Thirion, B. Uthuppu, Y. Hwang, M.H. Jakobsen, H.R. Andersen, C.T. Yavuz, *Covalent organic polymer functionalization of activated carbon surfaces through acyl chloride for environmental clean-up.* Chemical Engineering Journal, 309(2017) 766-771.

[18] N. Oladoja, R. Adelagun, A. Ahmad, E. Unuabonah, H. Bello, *Preparation of magnetic, macro-reticulated cross-linked chitosan for tetracycline removal from aquatic systems.* Colloids and Surfaces B: Biointerfaces, 117(2014) 51-59.

[19] S.-D. Pan, X.-H. Chen, H.-Y. Shen, X.-P. Li, M.-Q. Cai, Y.-G. Zhao, M.-C. Jin, *Rapid and effective sample cleanup based on graphene oxide-encapsulated core–shell magnetic microspheres for determination of fifteen trace environmental phenols in seafood by liquid chromatography–tandem mass spectrometry.* Analytica chimica acta, 919(2016) 34-46.

[20] S.-D. Pan, H.-Y. Shen, L.-X. Zhou, X.-H. Chen, Y.-G. Zhao, M.-Q. Cai, M.-C. Jin, *Controlled synthesis of pentachlorophenol-imprinted polymers on the surface of magnetic graphene oxide for highly selective adsorption.* Journal of Materials Chemistry A, 2(2014) 15345-15356.

[21] H.A. Patel, F. Karadas, A. Canlier, J. Park, E. Deniz, Y. Jung, M. Atilhan, C.T. Yavuz, *High capacity carbon dioxide adsorption by inexpensive covalent organic polymers.* Journal of Materials Chemistry, 22(2012) 8431-8437.

[22] P.D. Mines, J. Byun, Y. Hwang, H. Patel, H.R. Andersen, C. Yavuz, *Nanoporous networks as effective stabilisation matrices for nanoscale zero-valent iron and groundwater pollutant removal.* Journal of Materials Chemistry A, 4(2016) 632-639.

[23] H.A. Patel, M.S. Yavuz, C.T. Yavuz, *Exceptional organic solvent uptake by disulfide-linked polymeric networks.* RSC Advances, 4(2014) 24320-24323.

[24] Z. Ding, I. Bourven, G. Guibaud, E.D. Van Hullebusch, A. Panico, F. Pirozzi, G. Esposito, *Role of extracellular polymeric substances (EPS) production in bioaggregation: application to wastewater treatment.* Applied microbiology and biotechnology, 99(2015) 9883-9905.

[25] W. Chen, X. Gao, H. Xu, Y. Cai, J. Cui, *Influence of extracellular polymeric substances (EPS) treated by combined ultrasound pretreatment and chemical re-flocculation on water treatment sludge settling performance.* Chemosphere, 170(2017) 196-206.

[26] A. Singh, R.K. Sharma, M. Agrawal, F.M. Marshall, *Health risk assessment of heavy metals via dietary intake of foodstuffs from the wastewater irrigated site of a dry tropical area of India.* Food and Chemical Toxicology, 48(2010) 611-619.

[27] G.F.D.-W.Q. Who, *Health Criteria and Other Supporting Information*, W.H. Organization, Editor. 1998, addendum to Vol. 2: Geneva, Switzerland.

[28] S. Khan, Q. Cao, Y. Zheng, Y. Huang, Y. Zhu, *Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China.* Environmental pollution, 152(2008) 686-692.

[29] G. Wu, H. Kang, X. Zhang, H. Shao, L. Chu, C. Ruan, *A critical review on the bio-removal of hazardous heavy metals from contaminated soils: issues, progress, eco-environmental concerns and opportunities.* Journal of Hazardous Materials, 174(2010) 1-8.

[30] M.M. Lasat, A.J. Baker, L.V. Kochian, *Physiological characterization of root Zn2+ absorption and translocation to shoots in Zn hyperaccumulator and nonaccumulator species of Thlaspi.* Plant physiology, 112(1996) 1715-1722.

ACCEPTED MANUSCRIPT

[31] O.J. Hao, H. Kim, P.-C. Chiang, *Decolorization of wastewater*. Critical reviews in environmental science and technology, 30(2000) 449-505.

[32] U. Pagga ,D. Brown, *The degradation of dyestuffs: Part II Behaviour of dyestuffs in aerobic biodegradation tests*. Chemosphere, 15(1986) 479-491.

[33] R.S. Blackburn, *Natural polysaccharides and their interactions with dye molecules: applications in effluent treatment*. Environmental science & technology, 38(2004) 4905-4909.

[34] S. Vanhulle, M. Trovaslet, E. Enaud, M. Lucas, S. Taghavi, D. Van Der Lelie, B. Van Aken, M. Foret, R.C. Onderwater, D. Wesenberg, *Decolorization, cytotoxicity, and genotoxicity reduction during a combined ozonation/fungal treatment of dye-contaminated wastewater*. Environmental science & technology, 42(2007) 584-589.

[35] S. Pan, Y. Zhang, H. Shen, M. Hu, *An intensive study on the magnetic effect of mercapto-functionalized nano-magnetic Fe 3 O 4 polymers and their adsorption mechanism for the removal of Hg (II) from aqueous solution*. Chemical engineering journal, 210(2012) 564-574.

[36] H. Shen, S. Pan, Y. Zhang, X. Huang, H. Gong, *A new insight on the adsorption mechanism of amino-functionalized nano-Fe 3 O 4 magnetic polymers in Cu (II), Cr (VI) co-existing water system*. Chemical Engineering Journal, 183(2012) 180-191.

[37] M. Min, L. Shen, G. Hong, M. Zhu, Y. Zhang, X. Wang, Y. Chen, B.S. Hsiao, *Micro-nano structure poly (ether sulfones)/poly (ethyleneimine) nanofibrous affinity membranes for adsorption of anionic dyes and heavy metal ions in aqueous solution*. Chemical engineering journal, 197(2012) 88-100.

[38] G. Lofrano, M. Carotenuto, G. Libralato, R.F. Domingos, A. Markus, L. Dini, R.K. Gautam, D. Baldantoni, M. Rossi, S.K. Sharma, *Polymer functionalized nanocomposites for metals removal from water and wastewater: an overview*. Water research, 92(2016) 22-37.

[39] N. Shamim, L. Hong, K. Hidajat, M. Uddin, *Thermosensitive polymer (N-isopropylacrylamide) coated nanomagnetic particles: preparation and characterization*. Colloids and surfaces b: biointerfaces, 55(2007) 51-58.

[40] P.E. Molokwane, K.C. Meli, E.M. Nkhalambayausi-Chirwa, *Chromium (VI) reduction in activated sludge bacteria exposed to high chromium loading: Brits culture (South Africa)*. Water research, 42(2008) 4538-4548.

[41] S.-H. Huang ,D.-H. Chen, *Rapid removal of heavy metal cations and anions from aqueous solutions by an amino-functionalized magnetic nano-adsorbent*. Journal of Hazardous Materials, 163(2009) 174-179.

[42] J. Hu, G. Chen, I.M. Lo, *Selective removal of heavy metals from industrial wastewater using maghemite nanoparticle: performance and mechanisms*. Journal of environmental engineering, 132(2006) 709-715.

[43] Y.-G. Zhao, H.-Y. Shen, S.-D. Pan, M.-Q. Hu, *Synthesis, characterization and properties of ethylenediamine-functionalized Fe 3 O 4 magnetic polymers for removal of Cr (VI) in wastewater*. Journal of Hazardous Materials, 182(2010) 295-302.

[44] Y.-G. Zhao, H.-Y. Shen, S.-D. Pan, M.-Q. Hu, Q.-H. Xia, *Preparation and characterization of amino-functionalized nano-Fe3O4 magnetic polymer adsorbents for removal of chromium (VI) ions*. Journal of materials science, 45(2010) 5291-5301.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[45] H.H. Lara, N.V. Ayala-Núnez, L.D.C.I. Turrent, C.R. Padilla, *Bactericidal effect of silver nanoparticles against multidrug-resistant bacteria*. World Journal of Microbiology and Biotechnology, 26(2010) 615-621.

[46] S. Hanif ,A. Shahzad, *Removal of chromium (VI) and dye Alizarin Red S (ARS) using polymer-coated iron oxide (Fe3O4) magnetic nanoparticles by co-precipitation method*. Journal of nanoparticle research, 16(2014) 2429.

[47] M.-L. Chen, J.-Q. Min, S.-D. Pan, M.-C. Jin, *Surface core–shell magnetic polymer modified graphene oxide-based material for 2, 4, 6-trichlorophenol removal*. RSC Advances, 4(2014) 63494-63501.

[48] O. Akhavan, *Photocatalytic reduction of graphene oxides hybridized by ZnO nanoparticles in ethanol*. Carbon, 49(2011) 11-18.

[49] S.-D. Pan, L.-X. Zhou, Y.-G. Zhao, X.-H. Chen, H.-Y. Shen, M.-Q. Cai, M.-C. Jin, *Amine-functional magnetic polymer modified graphene oxide as magnetic solid-phase extraction materials combined with liquid chromatography–tandem mass spectrometry for chlorophenols analysis in environmental water*. Journal of Chromatography A, 1362(2014) 34-42.

[50] X. Zhu, Y. Zhu, S. Murali, M.D. Stoller, R.S. Ruoff, *Nanostructured reduced graphene oxide/Fe2O3 composite as a high-performance anode material for lithium ion batteries*. ACS nano, 5(2011) 3333-3338.

[51] L. Chen, S. Chai, K. Liu, N. Ning, J. Gao, Q. Liu, F. Chen, Q. Fu, *Enhanced epoxy/silica composites mechanical properties by introducing graphene oxide to the interface*. ACS applied materials & interfaces, 4(2012) 4398-4404.

[52] Z. Shi, J. Hu, Q. Li, S. Zhang, Y. Liang, H. Zhang, *Graphene based solid phase extraction combined with ultra high performance liquid chromatography–tandem mass spectrometry for carbamate pesticides analysis in environmental water samples*. Journal of Chromatography A, 1355(2014) 219-227.

[53] S.-D. Pan, X.-H. Chen, X.-P. Li, M.-Q. Cai, H.-Y. Shen, Y.-G. Zhao, M.-C. Jin, *In situ controllable synthesis of graphene oxide-based ternary magnetic molecularly imprinted polymer hybrid for efficient enrichment and detection of eight microcystins*. Journal of Materials Chemistry A, 3(2015) 23042-23052.

[54] S. Zhang, Z. Li, C. Wang, Z. Wang, *Cyclodextrin-functionalized reduced graphene oxide as a fiber coating material for the solid-phase microextraction of some volatile aromatic compounds*. Journal of separation science, 38(2015) 1711-1720.

[55] R. Liu, Y. Zhao, T. Chu, *Theoretical exploration of MgH 2 and graphene nano-flakes in cyclohexane: proposing a new perspective toward functional hydrogen storage material*. Chemical Communications, 51(2015) 2429-2432.

[56] S. Teixeira, N.S. Ferreira, R.S. Conlan, O. Guy, M.G.F. Sales, *Chitosan/AuNPs Modified Graphene Electrochemical Sensor for Label-Free Human Chorionic Gonadotropin Detection*. Electroanalysis, 26(2014) 2591-2598.

[57] X. Ma, H. Tao, K. Yang, L. Feng, L. Cheng, X. Shi, Y. Li, L. Guo, Z. Liu, *A functionalized graphene oxide-iron oxide nanocomposite for magnetically targeted drug delivery, photothermal therapy, and magnetic resonance imaging*. Nano Research, 5(2012) 199-212.

[58] C. He, J.J. Zhang, P.K. Shen, *Nitrogen-self-doped graphene-based non-precious metal catalyst with superior performance to Pt/C catalyst toward oxygen reduction reaction*. Journal of Materials Chemistry A, 2(2014) 3231-3236.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[59] H. Hashemipour, H. Kermanshahi, A. Golian, V. Khaksar, *Effects of carboxy methyl cellulose and thymol+ carvacrol on performance, digesta viscosity and some blood metabolites of broilers*. Journal of animal physiology and animal nutrition, 98(2014) 672-679.

[60] C. Xu, X. Shen, L. Ye, *Molecularly imprinted magnetic materials prepared from modular and clickable nanoparticles*. Journal of Materials Chemistry, 22(2012) 7427-7433.

[61] G. Sun, P. Wang, S. Ge, L. Ge, J. Yu, M. Yan, *Photoelectrochemical sensor for pentachlorophenol on microfluidic paper-based analytical device based on the molecular imprinting technique*. Biosensors and Bioelectronics, 56(2014) 97-103.

[62] R. Liu, M. Sha, S. Jiang, J. Luo, X. Liu, *A facile approach for imprinting protein on the surface of multi-walled carbon nanotubes*. Talanta, 120(2014) 76-83.

[63] S. Zhong, Y. Kong, L. Zhou, C. Zhou, X. Zhang, Y. Wang, *Efficient conversion of myricetin from Ampelopsis grossedentata extracts and its purification by MIP-SPE*. Journal of Chromatography B, 945(2014) 39-45.

[64] X. Yin, Q. Liu, X. Ma, X. Zhou, M. Zhao, P. Tu, *Correlation study between molecular structure of sesquiterpene lactones and the selective adsorption performance of molecularly imprinted polymers*. Journal of Chromatography A, 1354(2014) 9-17.

[65] B. Bhanvase, D. Pinjari, P. Gogate, S. Sonawane, A. Pandit, *Synthesis of exfoliated poly (styrene-co-methyl methacrylate)/montmorillonite nanocomposite using ultrasound assisted in situ emulsion copolymerization*. Chemical Engineering Journal, 181(2012) 770-778.

[66] M.R. Mauricio, M.R. Guilherme, M.H. Kunita, E.C. Muniz, A.F. Rubira, *Designing nanostructured microspheres with well-defined outlines by mixing carboxyl-functionalized amylose and magnetite via ultrasound*. Chemical engineering journal, 189(2012) 456-463.

[67] J.-H. Jang, C. Pak, Y.-U. Kwon, *Ultrasound-assisted polyol synthesis and electrocatalytic characterization of Pd x Co alloy and core–shell nanoparticles*. Journal of Power Sources, 201(2012) 179-183.

[68] Y. Yan, Q. An, Z. Xiao, W. Zheng, S. Zhai, *Flexible core-shell/bead-like alginate@ PEI with exceptional adsorption capacity, recycling performance toward batch and column sorption of Cr (VI)*. Chemical Engineering Journal, 313(2017) 475-486.

[69] S.-D. Pan, X.-H. Chen, X.-P. Li, M.-Q. Cai, H.-Y. Shen, Y.-G. Zhao, M.-C. Jin, *Double-sided magnetic molecularly imprinted polymer modified graphene oxide for highly efficient enrichment and fast detection of trace-level microcystins from large-volume water samples combined with liquid chromatography–tandem mass spectrometry*. Journal of Chromatography A, 1422(2015) 1-12.

[70] H. Yu, K.D. Clark, J.L. Anderson, *Rapid and sensitive analysis of microcystins using ionic liquid-based in situ dispersive liquid–liquid microextraction*. Journal of Chromatography A, 1406(2015) 10-18.

[71] W.M. Draper, D. Xu, P. Behniwal, M.J. Mckinney, P. Jayalath, J.S. Dhoot, D. Wijekoon, *Optimizing LC-MS-MS determination of microcystin toxins in natural water and drinking water supplies*. Analytical Methods, 5(2013) 6796-6806.

[72] E.A. Mbukwa, T.A. Msagati, B.B. Mamba, *Preparation of guanidinium terminus-molecularly imprinted polymers for selective recognition and solid-phase extraction (SPE) of [arginine]-microcystins*. Analytical and bioanalytical chemistry, 405(2013) 4253-4267.

[73] G. Crini, *Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment*. Progress in polymer science, 30(2005) 38-70.

ACCEPTED MANUSCRIPT

[74] M.N.R. Kumar, *A review of chitin and chitosan applications*. Reactive and functional polymers, 46(2000) 1-27.

[75] G. Crini, N. Morin-Crini, N. Fatin-Rouge, S. Deon, P. Fievet, *Metal removal from aqueous media by polymer-assisted ultrafiltration with chitosan*. Arabian Journal of Chemistry, 10(2017) S3826-S3839.

[76] N.A. Oladoja, E.I. Unuabonah, O.S. Amuda, O.M. Kolawole, *Polysaccharides as a Green and Sustainable Resources for Water and Wastewater Treatment*. 2017: Springer.

[77] A.J. Sami, M. Khalid, S. Iqbal, M. Afzal, A. Shakoori, *Synthesis and Application of Chitosan-Starch Based Nanocomposite in Wastewater Treatment for the Removal of Anionic Commercial Dyes*. Pakistan Journal of Zoology, 49(2017) 21-21.

[78] N. Erhunmwunse ,M. Ainerua, *Characterization of some blood parameters of African Catfish (Clarias gariepinus)*. Am Eurasian J Toxicol Sci, 5(2013) 72-76.

[79] B. Krajewska, *Diffusion of metal ions through gel chitosan membranes*. Reactive and Functional Polymers, 47(2001) 37-47.

[80] W. Kaminski, E. Tomczak, K. Jaros, *Interactions of metal ions sorbed on chitosan beads*. Desalination, 218(2008) 281-286.

[81] B.J. Mcafee, W.D. Gould, J.C. Nadeau, A.C. Da Costa, *Biosorption of metal ions using chitosan, chitin, and biomass of Rhizopus oryzae*. Separation Science and technology, 36(2001) 3207-3222.

[82] F.-L. Mi, S.-S. Shyu, C.-T. Chen, J.-Y. Lai, *Adsorption of indomethacin onto chemically modified chitosan beads*. Polymer, 43(2002) 757-765.

[83] F. Delval, G. Crini, J. Vebrel, M. Knorr, G. Sauvin, E. Conte. *Starch-modified filters used for the removal of dyes from waste water*. in *Macromolecular Symposia*. 2003. Wiley Online Library.

[84] Z. Xing, Z. Ju, J. Yang, H. Xu, Y. Qian, *One-step solid state reaction to selectively fabricate cubic and tetragonal CuFe 2 O 4 anode material for high power lithium ion batteries*. Electrochimica Acta, 102(2013) 51-57.

[85] S.K. Nadavala, K. Swayampakula, V.M. Boddu, K. Abburi, *Biosorption of phenol and o-chlorophenol from aqueous solutions on to chitosan–calcium alginate blended beads*. Journal of Hazardous Materials, 162(2009) 482-489.

[86] F. Marrakchi, W. Khanday, M. Asif, B. Hameed, *Cross-linked chitosan/sepiolite composite for the adsorption of methylene blue and reactive orange 16*. International journal of biological macromolecules, 93(2016) 1231-1239.

[87] P.E. Hovsepian, D. Lewis, W. Münz, S. Lyon, M. Tomlinson, *Combined cathodic arc/unbalanced magnetron grown CrN/NbN superlattice coatings for corrosion resistant applications*. Surface and Coatings Technology, 120(1999) 535-541.

[88] Y. Yao, B. Gao, J. Fang, M. Zhang, H. Chen, Y. Zhou, A.E. Creamer, Y. Sun, L. Yang, *Characterization and environmental applications of clay–biochar composites*. Chemical Engineering Journal, 242(2014) 136-143.

[89] H. Karaer ,İ. Uzun, *Adsorption of basic dyestuffs from aqueous solution by modified chitosan*. Desalination and Water Treatment, 51(2013) 2294-2305.

[90] L. Zeng, M. Xie, Q. Zhang, Y. Kang, X. Guo, H. Xiao, Y. Peng, J. Luo, *Chitosan/organic rectorite composite for the magnetic uptake of methylene blue and methyl orange*. Carbohydrate polymers, 123(2015) 89-98.

[91] J. Xie, C. Li, L. Chi, D. Wu, *Chitosan modified zeolite as a versatile adsorbent for the removal of different pollutants from water*. Fuel, 103(2013) 480-485.

ACCEPTED MANUSCRIPT

[92] J.-P. Wang, Y.-Z. Chen, S.-J. Yuan, G.-P. Sheng, H.-Q. Yu, *Synthesis and characterization of a novel cationic chitosan-based flocculant with a high water-solubility for pulp mill wastewater treatment.* Water research, 43(2009) 5267-5275.

[93] Y.C. Chang ,D.H. Chen, *Adsorption Kinetics and Thermodynamics of Acid Dyes on a Carboxymethylated Chitosan-Conjugated Magnetic Nano-Adsorbent.* Macromolecular bioscience, 5(2005) 254-261.

[94] C.-Y. Chen, C.-C. Chen, Y.-C. Chung, *Removal of phthalate esters by α-cyclodextrin-linked chitosan bead.* Bioresource Technology, 98(2007) 2578-2583.

[95] A.Z.M. Badruddoza, Z.B.Z. Shawon, W.J.D. Tay, K. Hidajat, M.S. Uddin, *Fe 3 O 4/cyclodextrin polymer nanocomposites for selective heavy metals removal from industrial wastewater*. Carbohydrate polymers, 91(2013) 322-332.

[96] L. Yu, W. Xue, L. Cui, W. Xing, X. Cao, H. Li, *Use of hydroxypropyl-β-cyclodextrin/polyethylene glycol 400, modified Fe 3 O 4 nanoparticles for congo red removal*. International journal of biological macromolecules, 64(2014) 233-239.

[97] R. Mirzajani, N. Pourreza, S.S.A. Najjar, *β-Cyclodextrin-based polyurethane (β-CDPU) polymers as solid media for adsorption and determination of Pb (II) ions in dust and water samples*. Research on Chemical Intermediates, 40(2014) 2667-2679.

[98] G. Crini ,M. Morcellet, *Synthesis and applications of adsorbents containing cyclodextrins.* Journal of Separation Science, 25(2002) 789-813.

[99] N. Morin-Crini ,G. Crini, *Environmental applications of water-insoluble β-cyclodextrin–epichlorohydrin polymers.* Progress in Polymer Science, 38(2013) 344-368.

[100] K. Salipira, B. Mamba, R. Krause, T. Malefetse, S. Durbach, *Carbon nanotubes and cyclodextrin polymers for removing organic pollutants from water.* Environmental Chemistry Letters, 5(2007) 13-17.

[101] J. Re Mie Charles, G. Gorio Crini, N. Morin-Crini, P.-M. Badot, G. Trunfio, B. Sancey, M. De Carvalho, C. Bradu, S. Avramescu, P. Winterton, *Journal of the Taiwan Institute of Chemical Engineers.* (2013).

[102] G. Crini, *Kinetic and equilibrium studies on the removal of cationic dyes from aqueous solution by adsorption onto a cyclodextrin polymer.* Dyes and Pigments, 77(2008) 415-426.

[103] É. Euvrard, N. Morin-Crini, C. Druart, J. Bugnet, B. Martel, C. Cosentino, V. Moutarlier, G. Crini, *Cross-linked cyclodextrin-based material for treatment of metals and organic substances present in industrial discharge waters.* Beilstein journal of organic chemistry, 12(2016) 1826.

[104] R.M. Kakhki, *Application of magnetic nanoparticles modified with cyclodextrins as efficient adsorbents in separation systems.* Journal of Inclusion Phenomena and Macrocyclic Chemistry, 82(2015) 301-310.

[105] Q. Wu, C. Feng, C. Wang, Z. Wang, *A facile one-pot solvothermal method to produce superparamagnetic graphene–Fe 3 O 4 nanocomposite and its application in the removal of dye from aqueous solution*. Colloids and Surfaces B: Biointerfaces, 101(2013) 210-214.

[106] M.A. Sánchez-Trujillo, S. Lacorte, J. Villaverde, C. Barata, E. Morillo, *Decontamination of polycyclic aromatic hydrocarbons and nonylphenol from sewage sludge using hydroxypropyl-β-cyclodextrin and evaluation of the toxicity of leachates*. Environmental Science and Pollution Research, 21(2014) 507-517.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[107] D. Ko, J.S. Lee, H.A. Patel, M.H. Jakobsen, Y. Hwang, C.T. Yavuz, H.C.B. Hansen, H.R. Andersen, *Selective removal of heavy metal ions by disulfide linked polymer networks*. Journal of Hazardous Materials, 332(2017) 140-148.

[108] D. Ko, H.A. Patel, C.T. Yavuz, *Synthesis of nanoporous 1, 2, 4-oxadiazole networks with high CO 2 capture capacity*. Chemical Communications, 51(2015) 2915-2917.

[109] H.A. Patel, F. Karadas, J. Byun, J. Park, E. Deniz, A. Canlier, Y. Jung, M. Atilhan, C.T. Yavuz, *Highly Stable Nanoporous Sulfur-Bridged Covalent Organic Polymers for Carbon Dioxide Removal*. Advanced Functional Materials, 23(2013) 2270-2276.

[110] H.A. Patel, S.H. Je, J. Park, D.P. Chen, Y. Jung, C.T. Yavuz, A. Coskun, *Unprecedented high-temperature CO2 selectivity in N2-phobic nanoporous covalent organic polymers*. Nature communications, 4(2013) 1357.

[111] Z. Xiang, R. Mercado, J.M. Huck, H. Wang, Z. Guo, W. Wang, D. Cao, M. Haranczyk, B. Smit, *Systematic tuning and multifunctionalization of covalent organic polymers for enhanced carbon capture*. Journal of the American Chemical Society, 137(2015) 13301-13307.

[112] O. Koçer ,B. Acemioğlu, *Adsorption of Basic green 4 from aqueous solution by olive pomace and commercial activated carbon: process design, isotherm, kinetic and thermodynamic studies*. Desalination and Water Treatment, 57(2016) 16653-16669.

[113] R. Crane ,T. Scott, *Nanoscale zero-valent iron: future prospects for an emerging water treatment technology*. Journal of hazardous materials, 211(2012) 112-125.

[114] P.D. Mines, J. Byun, Y. Hwang, H. Patel, H.R. Andersen, C.T. Yavuz. *Nano-Sized Zero Valent Iron and Covalent Organic Polymer Composites for Azo Dye Remediation*. in *Nanotech MEET 2014*. 2014.

[115] F. Meinel, A. Ruhl, A. Sperlich, F. Zietzschmann, M. Jekel, *Pilot-scale investigation of micropollutant removal with granular and powdered activated carbon*. Water, Air, & Soil Pollution, 226(2015) 2260.

[116] P. D'abzac, F. Bordas, E. Van Hullebusch, P.N. Lens, G. Guibaud, *Extraction of extracellular polymeric substances (EPS) from anaerobic granular sludges: comparison of chemical and physical extraction protocols*. Applied microbiology and biotechnology, 85(2010) 1589-1599.

[117] Y. Shi, J. Huang, G. Zeng, Y. Gu, Y. Chen, Y. Hu, B. Tang, J. Zhou, Y. Yang, L. Shi, *Exploiting extracellular polymeric substances (EPS) controlling strategies for performance enhancement of biological wastewater treatments: An overview*. Chemosphere, (2017).

[118] H. Lin, M. Zhang, F. Wang, F. Meng, B.-Q. Liao, H. Hong, J. Chen, W. Gao, *A critical review of extracellular polymeric substances (EPSs) in membrane bioreactors: characteristics, roles in membrane fouling and control strategies*. Journal of Membrane science, 460(2014) 110-125.

[119] D. Yuan, Y. Wang, X. Qian, *Variations of internal structure and moisture distribution in activated sludge with stratified extracellular polymeric substances extraction*. International Biodeterioration & Biodegradation, 116(2017) 1-9.

[120] P. Zhang, F. Fang, Y.-P. Chen, Y. Shen, W. Zhang, J.-X. Yang, C. Li, J.-S. Guo, S.-Y. Liu, Y. Huang, *Composition of EPS fractions from suspended sludge and biofilm and their roles in microbial cell aggregation*. Chemosphere, 117(2014) 59-65.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[121] Y. Wang, J. Qin, S. Zhou, X. Lin, L. Ye, C. Song, Y. Yan, *Identification of the function of extracellular polymeric substances (EPS) in denitrifying phosphorus removal sludge in the presence of copper ion*. water research, 73(2015) 252-264.

[122] Y. Wang, G. Guo, H. Wang, T. Stephenson, J. Guo, L. Ye, *Long-term impact of anaerobic reaction time on the performance and granular characteristics of granular denitrifying biological phosphorus removal systems*. Water research, 47(2013) 5326-5337.

[123] G.-P. Sheng, J. Xu, H.-W. Luo, W.-W. Li, W.-H. Li, H.-Q. Yu, Z. Xie, S.-Q. Wei, F.-C. Hu, *Thermodynamic analysis on the binding of heavy metals onto extracellular polymeric substances (EPS) of activated sludge*. Water research, 47(2013) 607-614.

[124] F. Kang ,D. Zhu, *Abiotic reduction of 1, 3-dinitrobenzene by aqueous dissolved extracellular polymeric substances produced by microorganisms*. Journal of environmental quality, 42(2013) 1441-1448.

[125] X. Zhang, C.-W. Yang, H.-Q. Yu, G.-P. Sheng, *Light-induced reduction of silver ions to silver nanoparticles in aquatic environments by microbial extracellular polymeric substances (EPS)*. Water research, 106(2016) 242-248.

[126] R.L. Tate Iii ,M. Alexander, *Stability of Nitrosamines in Samples of Lake Water, Soil, and Sewage 2*. Journal of the National Cancer Institute, 54(1975) 327-330.

[127] Y. Yin, J. Liu, G. Jiang, *Sunlight-induced reduction of ionic Ag and Au to metallic nanoparticles by dissolved organic matter*. (2012).

[128] H. Flemming ,J. Wingender, *The biofilm matrix. Nat Rev Microbiol 8: 623–633*. (2010).

[129] H.-C. Flemming, J. Wingender, U. Szewzyk, P. Steinberg, S.A. Rice, S. Kjelleberg, *Biofilms: an emergent form of bacterial life*. Nature Reviews Microbiology, 14(2016) 563-575.

[130] J.D. Shrout ,R. Nerenberg, *Monitoring bacterial twitter: does quorum sensing determine the behavior of water and wastewater treatment biofilms?* Environmental science & technology, 46(2012) 1995-2005.

[131] J. Huang, Y. Shi, G. Zeng, Y. Gu, G. Chen, L. Shi, Y. Hu, B. Tang, J. Zhou, *Acyl-homoserine lactone-based quorum sensing and quorum quenching hold promise to determine the performance of biological wastewater treatments: an overview*. Chemosphere, 157(2016) 137-151.

[132] P. Tielen, H. Kuhn, F. Rosenau, K.-E. Jaeger, H.-C. Flemming, J. Wingender, *Interaction between extracellular lipase LipA and the polysaccharide alginate of Pseudomonas aeruginosa*. BMC microbiology, 13(2013) 159.

[133] J. Xu, G.-P. Sheng, Y. Ma, L.-F. Wang, H.-Q. Yu, *Roles of extracellular polymeric substances (EPS) in the migration and removal of sulfamethazine in activated sludge system*. Water research, 47(2013) 5298-5306.

[134] F. Gómez-Galván, L. Pérez-Álvarez, J. Matas, A. Álvarez-Bautista, J. Poejo, C.M. Duarte, L. Ruiz-Rubio, J.L. Vila-Vilela, L.M. León, *Preparation and characterization of soluble branched ionic β-cyclodextrins and their inclusion complexes with triclosan*. Carbohydrate polymers, 142(2016) 149-157.

[135] C. Gong, J. Jiang, D.A. Li, *Ultrasound coupled with Fenton oxidation pre-treatment of sludge to release organic carbon, nitrogen and phosphorus*. Science of the Total Environment, 532(2015) 495-500.

[136] P. Wolski ,I. Zawieja, *Effect of ultrasound field on dewatering of sewage sludge*. Archives of Environmental Protection, 38(2012) 25-31.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[137] P.L. Drake ,K.J. Hazelwood, *Exposure-related health effects of silver and silver compounds: a review*. The Annals of occupational hygiene, 49(2005) 575-585.

[138] H. Liu, J. Yang, N. Zhu, H. Zhang, Y. Li, S. He, C. Yang, H. Yao, *A comprehensive insight into the combined effects of Fenton's reagent and skeleton builders on sludge deep dewatering performance*. Journal of hazardous materials, 258(2013) 144-150.

[139] H. Xu, K. Shen, T. Ding, J. Cui, M. Ding, C. Lu, *Dewatering of drinking water treatment sludge using the Fenton-like process induced by electro-osmosis*. Chemical Engineering Journal, 293(2016) 207-215.

[140] H. Lin, M. Zhang, F. Wang, Y. He, J. Chen, H. Hong, A. Wang, H. Yu, *Experimental evidence for osmotic pressure-induced fouling in a membrane bioreactor*. Bioresource technology, 158(2014) 119-126.

[141] L. Deng, *Development of specific membrane bioreactors for membrane fouling control during wastewater treatment for reuse*. 2015.

[142] J. Ye, H. Li, C. Zhang, C. Ye, W. Han, *Classification and extraction methods of the clog components of constructed wetland*. Ecological engineering, 70(2014) 327-331.

[143] G. Fu, J. Zhang, W. Chen, Z. Chen, *Medium clogging and the dynamics of organic matter accumulation in constructed wetlands*. Ecological engineering, 60(2013) 393-398.

[144] G. Hua, W. Zhu, J. Shen, Y. Zhang, Y. Zeng, *The role of biofilm in clogging process in vertical flow constructed wetland*. Applied engineering in agriculture, 29(2013) 61-66.

[145] J. Nivala, P. Knowles, G. Dotro, J. García, S. Wallace, *Clogging in subsurface-flow treatment wetlands: measurement, modeling and management*. Water research, 46(2012) 1625-1640.

[146] H. Guofen, Z. Wei, Z. Lianfang, Z. Yunhui, *Applying solubilization treatment to reverse clogging in laboratory-scale vertical flow constructed wetlands*. Water Science and Technology, 61(2010) 1479-1487.

[147] M. Du, D. Xu, X. Trinh, S. Liu, M. Wang, Y. Zhang, J. Wu, Q. Zhou, Z. Wu, *EPS solubilization treatment by applying the biosurfactant rhamnolipid to reduce clogging in constructed wetlands*. Bioresource technology, 218(2016) 833-841.

[148] K.L. Larsen, *Large cyclodextrins*. Journal of inclusion phenomena and macrocyclic chemistry, 43(2002) 1-13.

[149] G. Astray, C. Gonzalez-Barreiro, J. Mejuto, R. Rial-Otero, J. Simal-Gándara, *A review on the use of cyclodextrins in foods*. Food Hydrocolloids, 23(2009) 1631-1640.

[150] L. Bardi, A. Mattei, S. Steffan, M. Marzona, *Hydrocarbon degradation by a soil microbial population with β-cyclodextrin as surfactant to enhance bioavailability*. Enzyme and Microbial technology, 27(2000) 709-713.

[151] S.-K. Kim ,N. Rajapakse, *Enzymatic production and biological activities of chitosan oligosaccharides (COS): A review*. Carbohydrate polymers, 62(2005) 357-368.

[152] R. Divakaran ,V.S. Pillai, *Flocculation of algae using chitosan*. Journal of Applied Phycology, 14(2002) 419-422.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

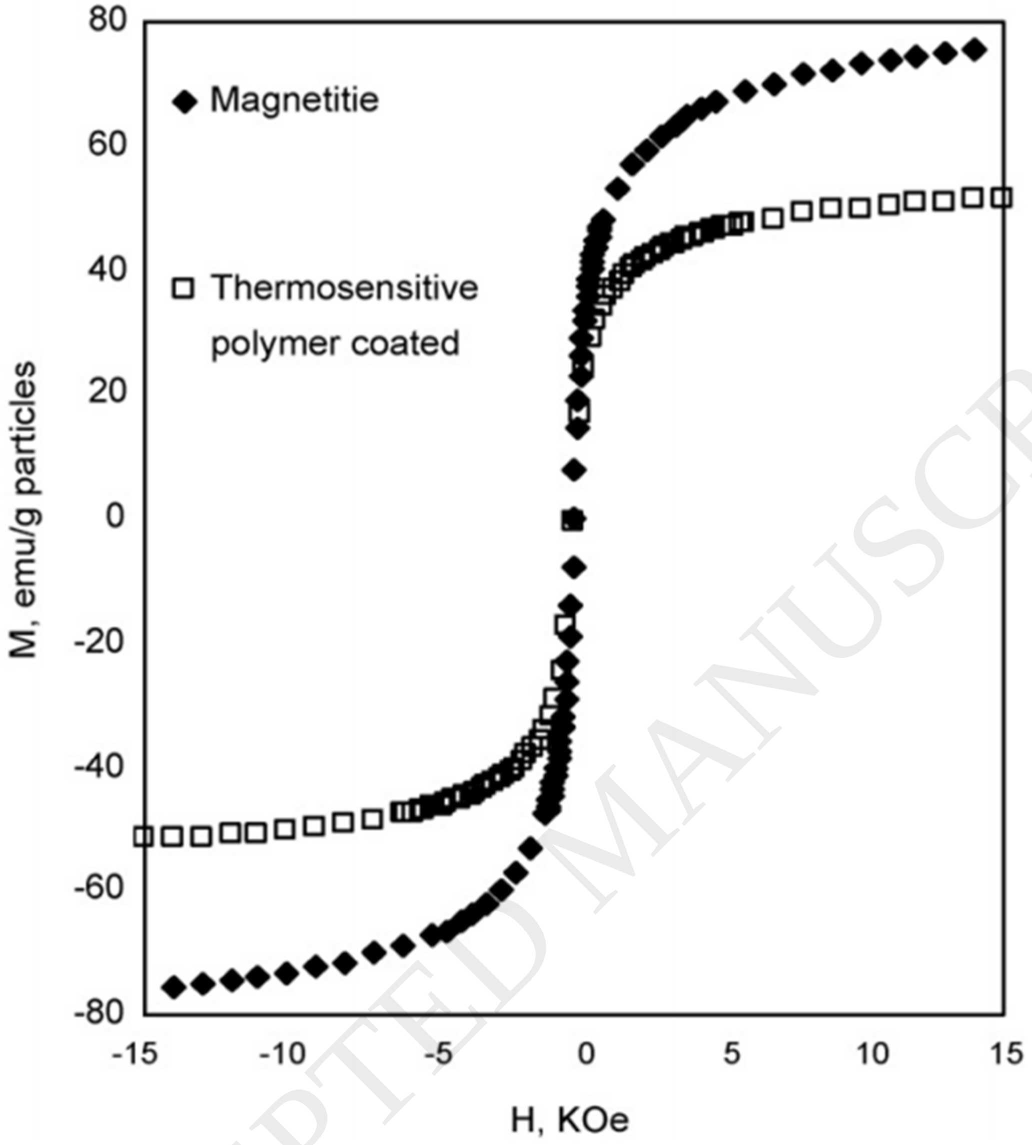


Fig. 1. VSM magnetization curve NMP adsorbent at room temperature [39].

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

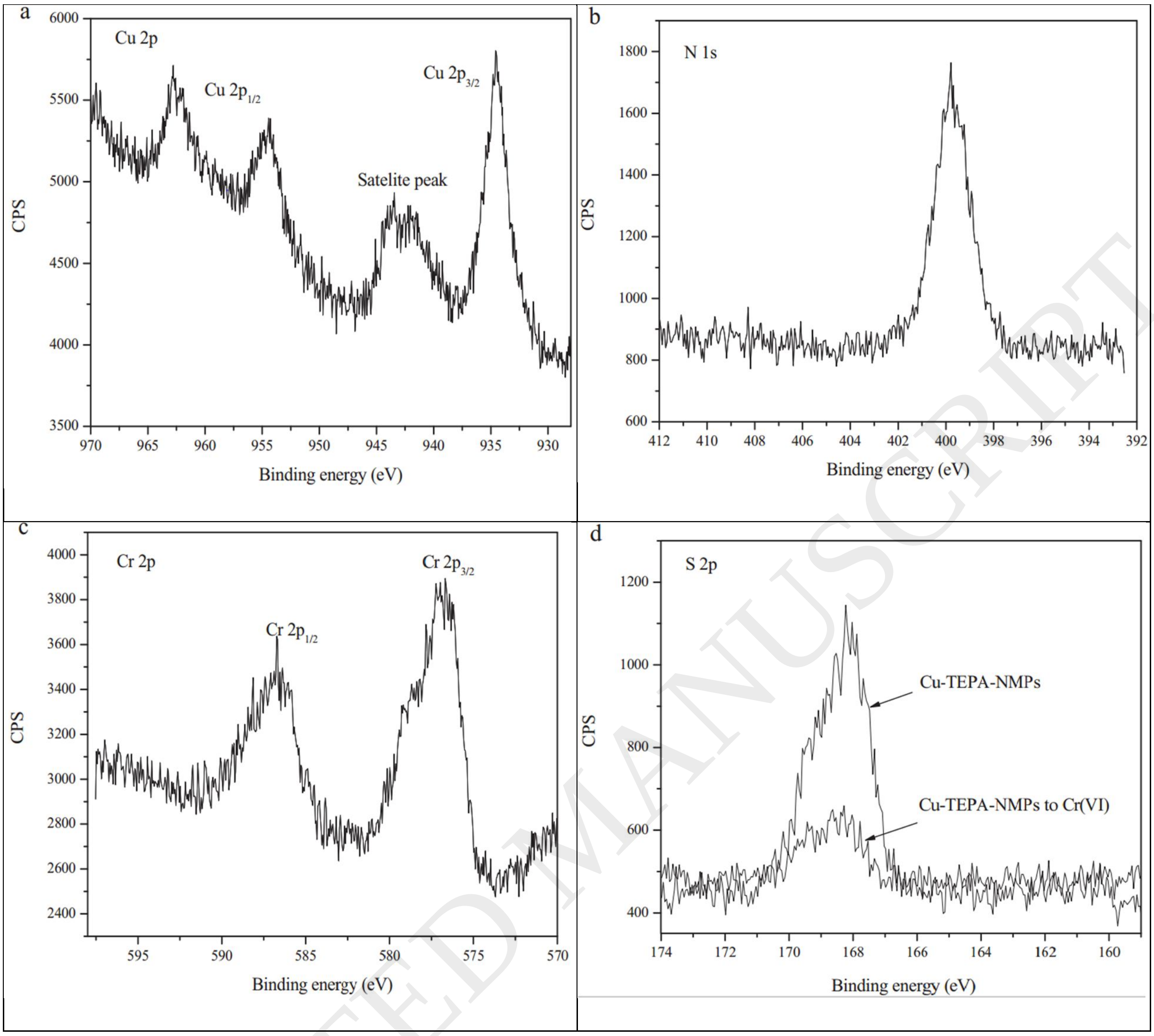


Fig. 2. XPS analysis of (a) Cu 2p, (b) N 1s, (c) Cr 2p, and (d) S 2p of Cu-TEPA-NMPs [36].

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

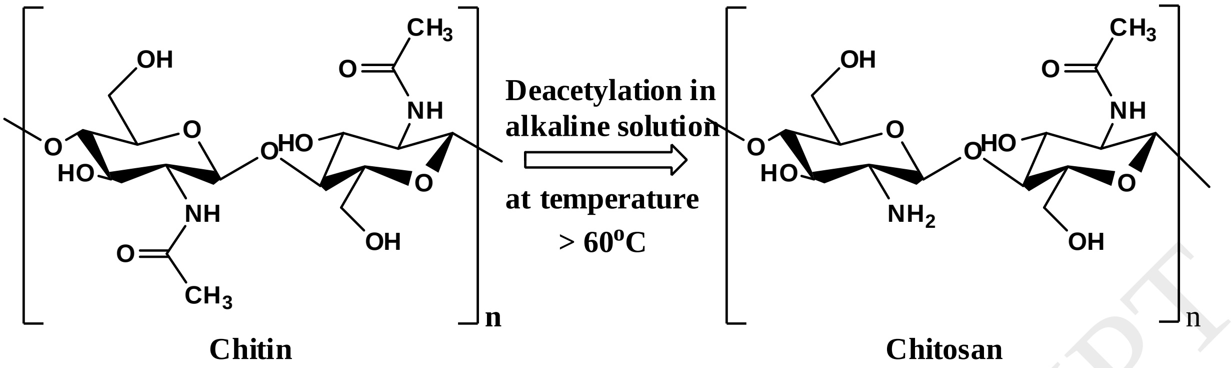


Figure 3: Conversion of Chitin to Chitosan.

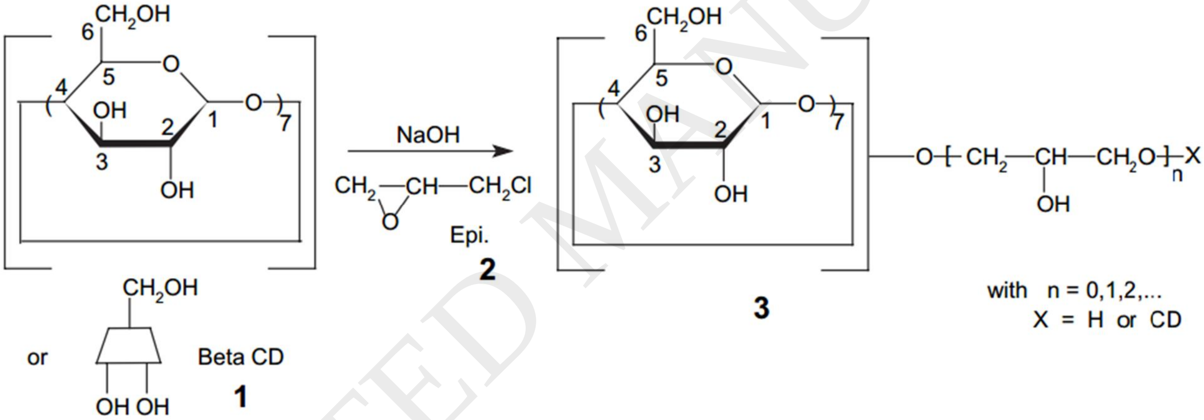


Fig. 4. Synthesis of crosslinked CD-based polymers [98].

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

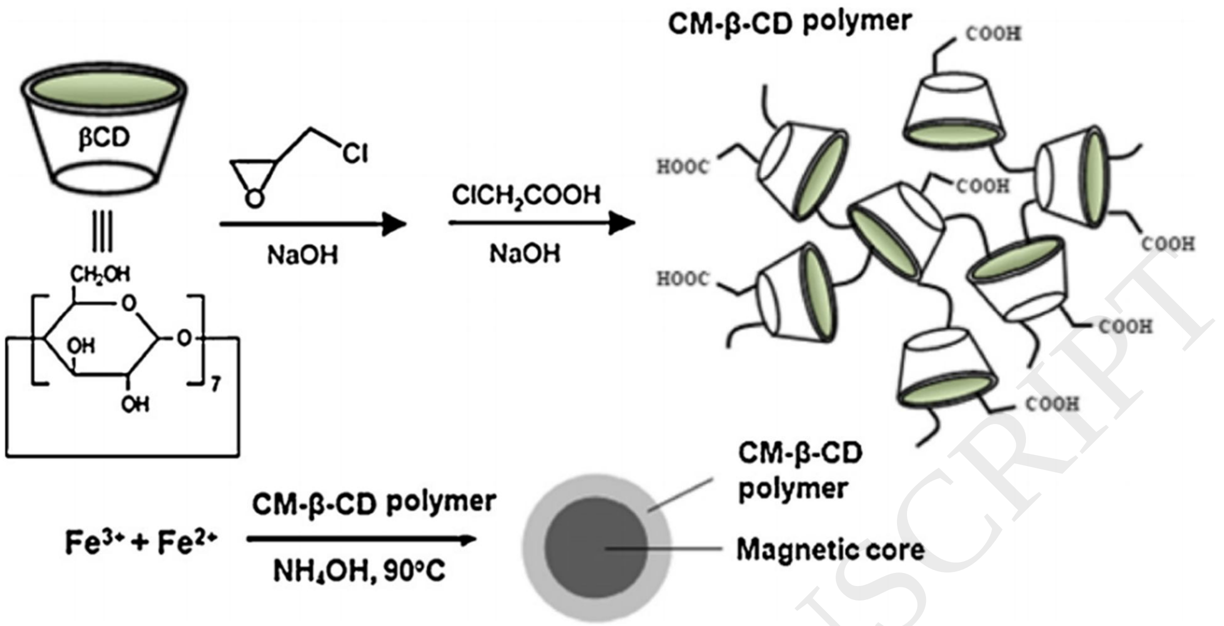


Figure 5. Schematic presentation of CM- β -CD polymer grafting on Fe3O4 nanoparticles [95].

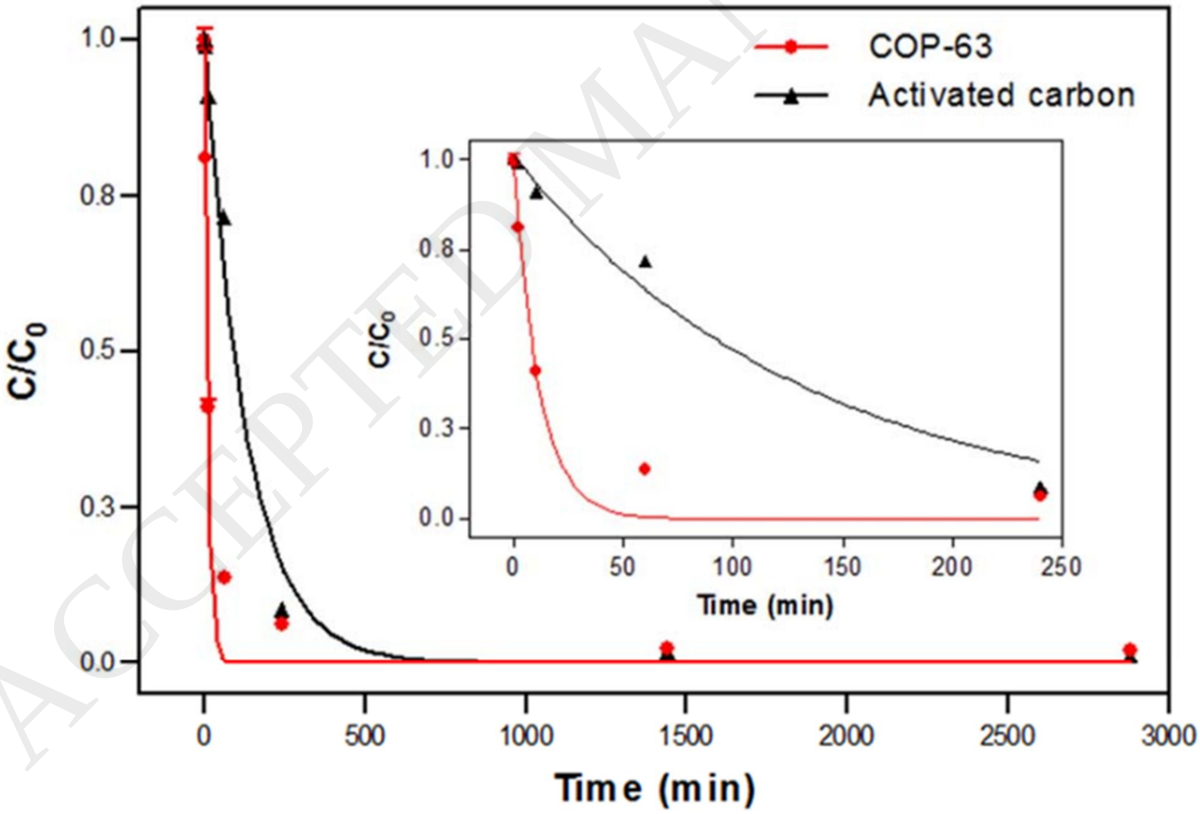


Figure 6. Kinetics of cadmium sorption to COP-63 and AC (Removal of cadmium in solution plotted versus time and lines dues to fitting by the first-order kinetic mode) 107].

ACCEPTED MANUSCRIPT

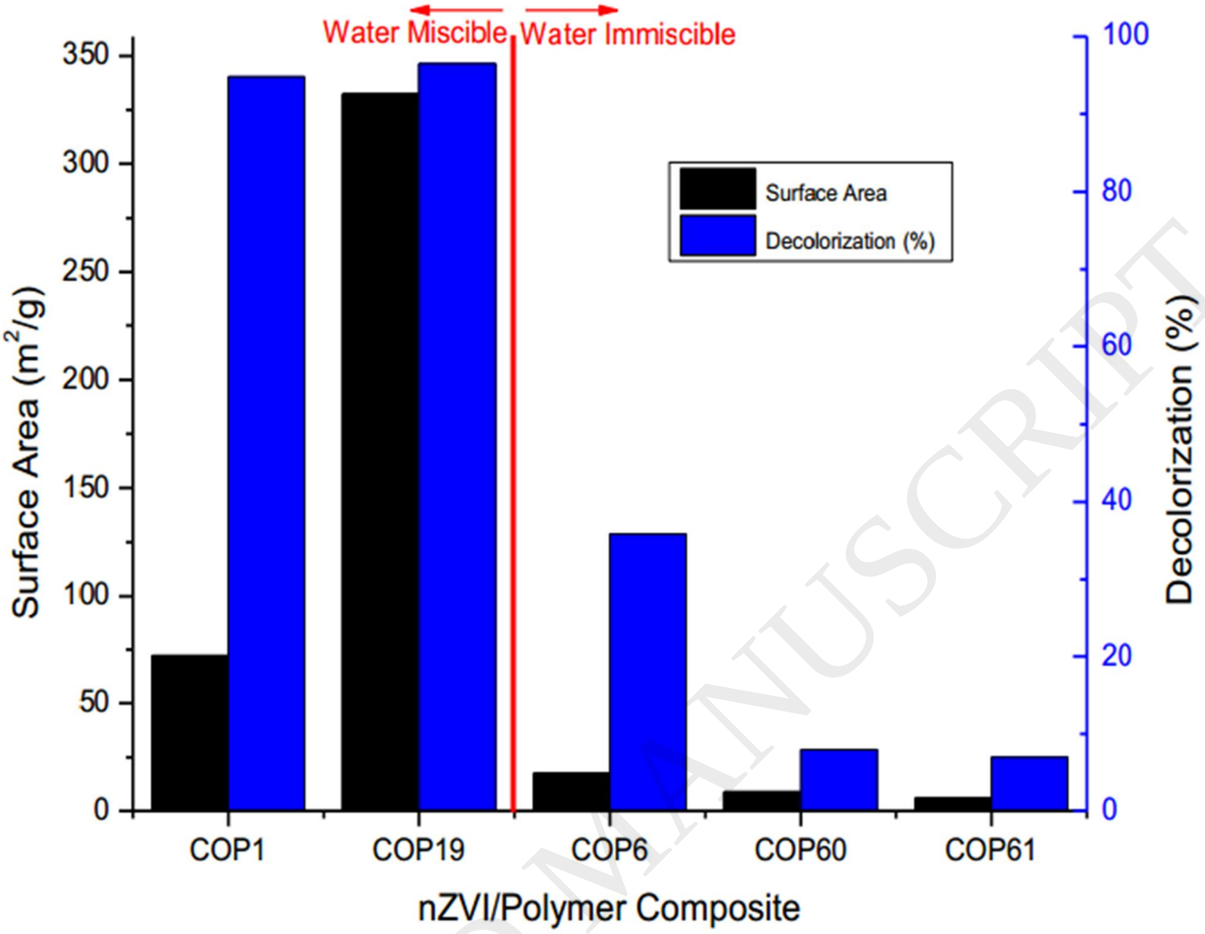


Figure 7. Relationship of composite surface area with decolorization of naphthol blue black ability, in terms of removal percentage, organized by water miscibility [114].

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

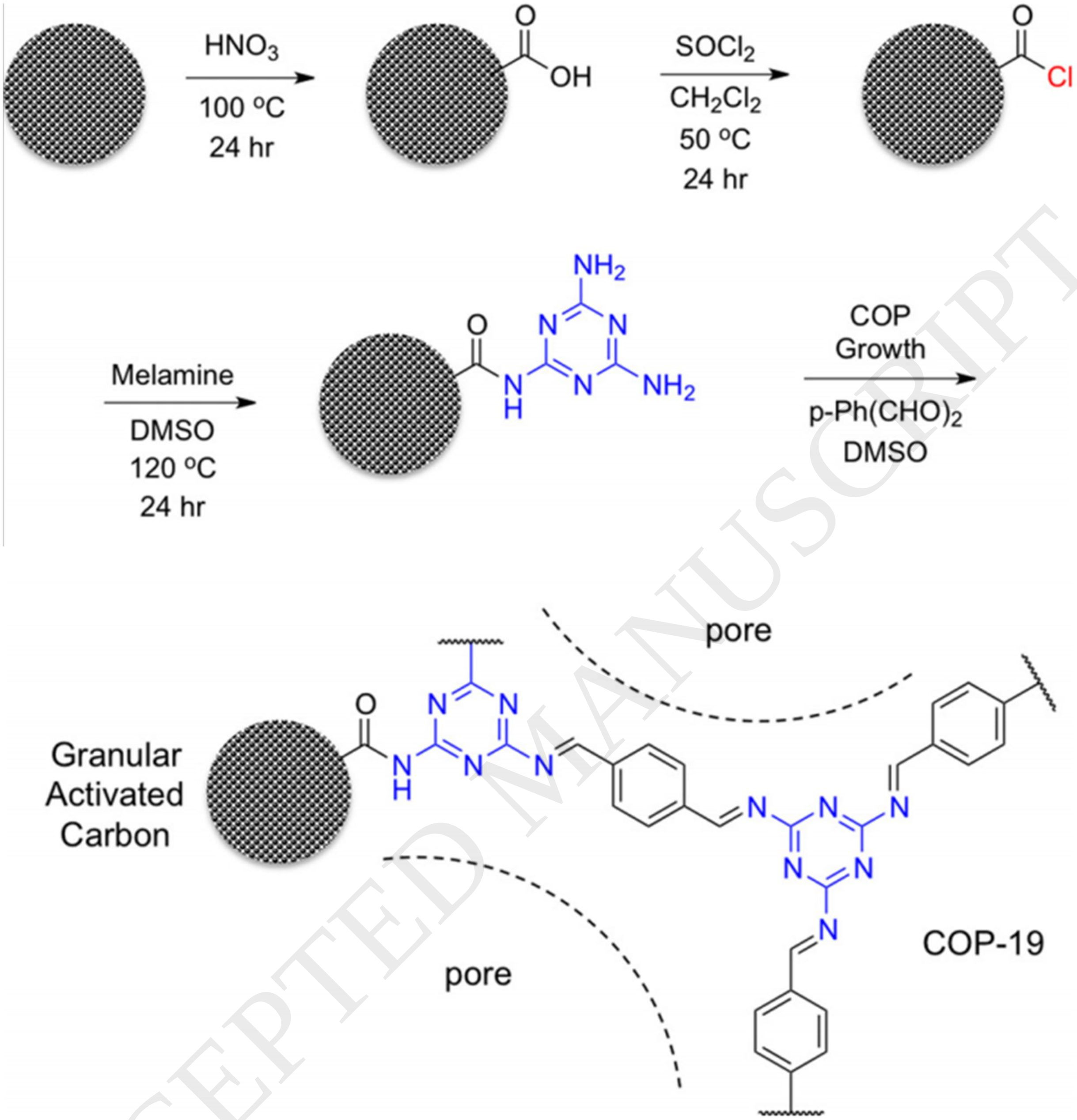


Fig. 8. Step-wise evolution of the COP attachment to the surface of activated carbon [17].

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

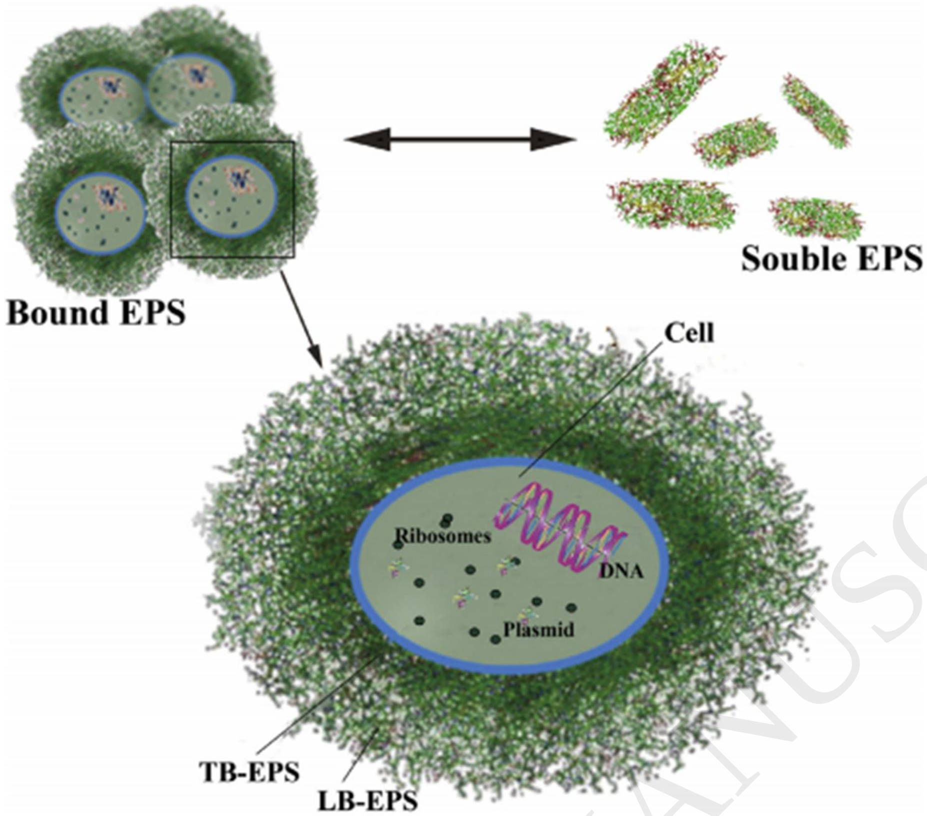


Fig. 9. Schematic of extracellular polymeric substances (EPS) structure [117].

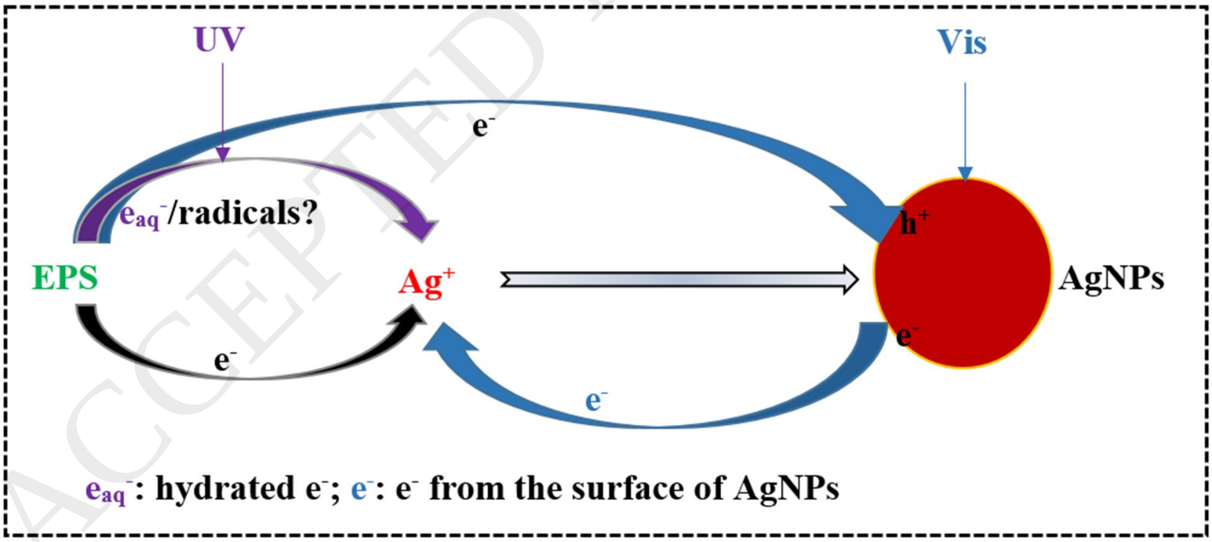
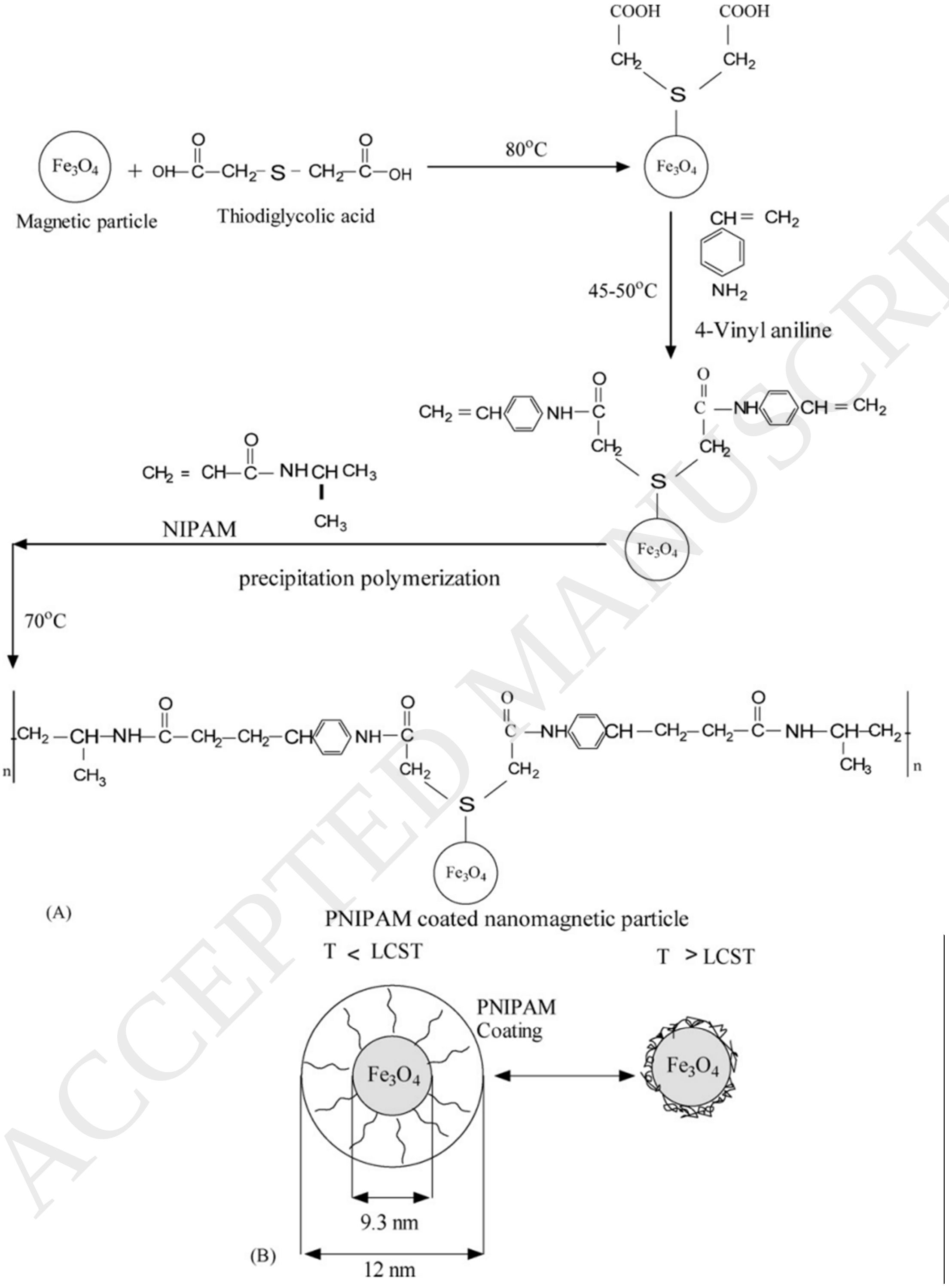


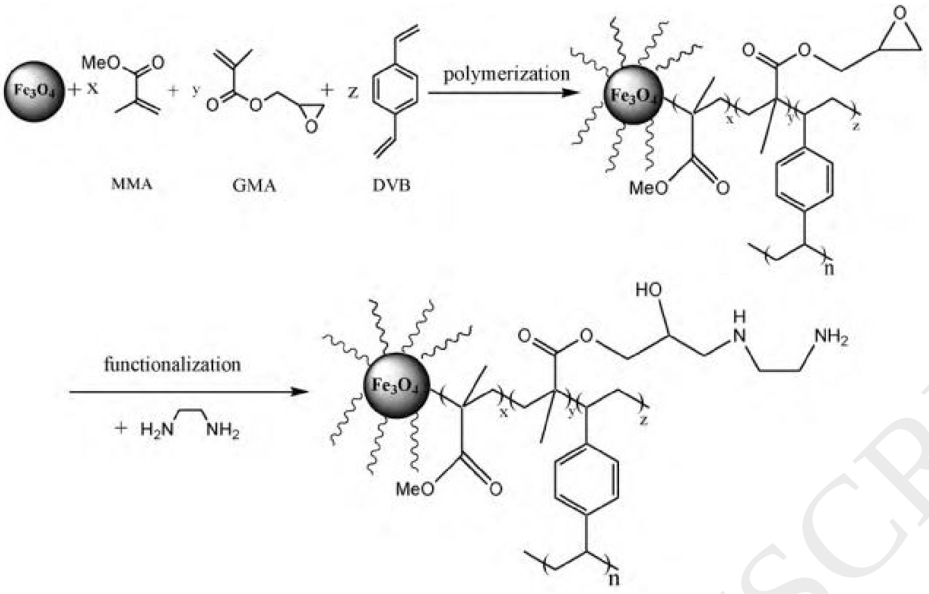
Fig. 10. Proposed mechanism of the effect of visible and UV light on the reduction of Ag^+ by EPS [125].

ACCEPTED MANUSCRIPT

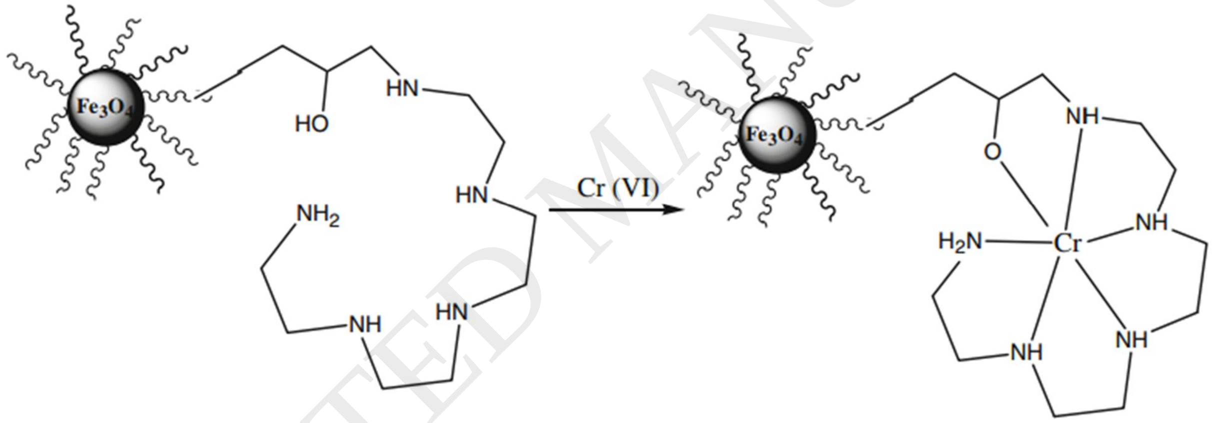
ACCEPTED MANUSCRIPT



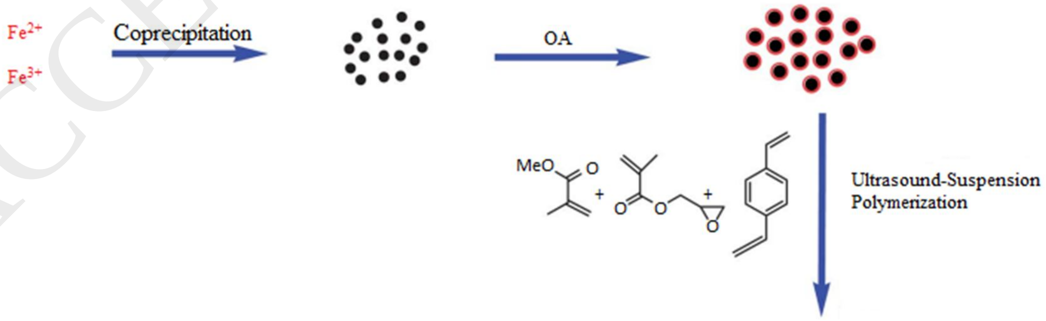
Scheme 1. Preparation of thermosensitive (PNIPAM) coated nanomagnetic particles (A) and schematic illustration of PNIPAM coated nanoparticles (B) [39].



Scheme 2. Amino-functionalization procedure of EDA-MPs [43].

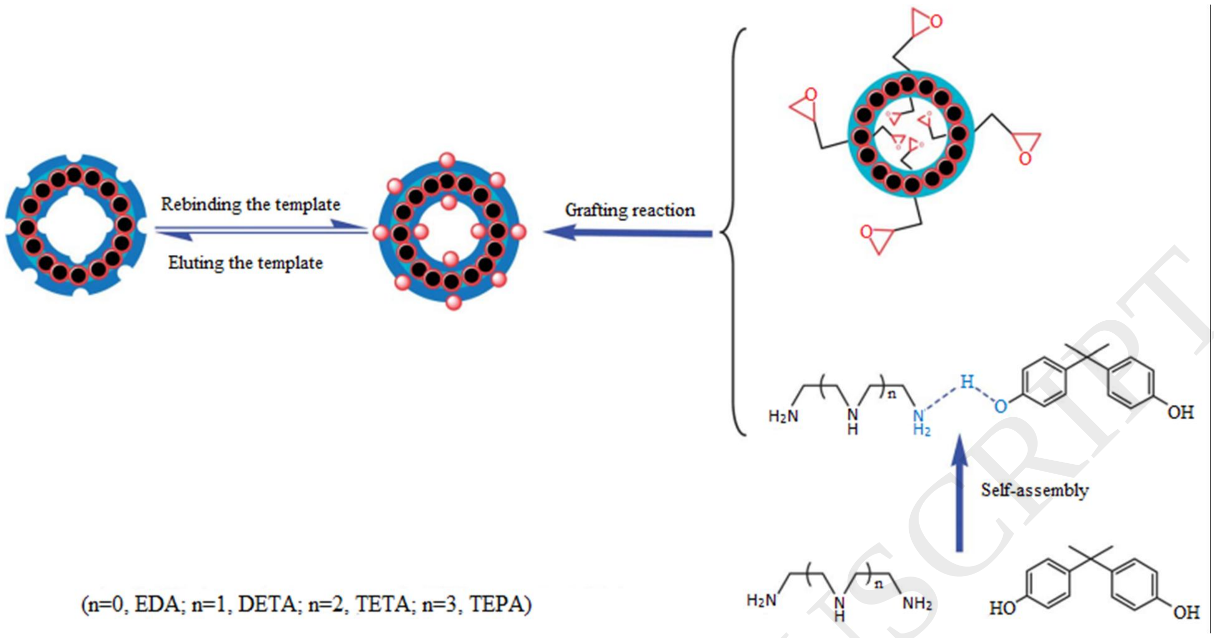


Scheme 3. The presumed process of the coordination interactions for the removal of Cr(VI) by TEPA-NMPs [44].



ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT



Scheme 4 Schematic procedure of the self-assembly of surface bisphenol A-imprinted CS-NR-Mag-MIP nanoparticles.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Table 1. Adsorption performance of several NMPs based on their preparation method and Fe_3O_4/monomer.

Sample	Description	Fe_3O_4/monomer	Monomer	Method	Surface area (m^2/g)	Pore volume (m^3/g)	Pore size (nm)	Adsorbate	Adsorption capacity (q_m) (mg/g)	Ref.
PNIPAM-NMP	polymer (N-isopropylacrylamide) coated nanomagnetic particles	1:0.3 g/g	N-isopropylacrylamide	Seed polymerization			12	BSA (0.5–2 mg/ml)	104 at 40 °C	[39]
EDA-MPs	Ethylenediamine-functionalized magnetic polymers	3.3% (1 g Fe_3O_4, 2 mL GMA, 4 mL MMA, 2 mL DVB)	GMA, MMA and DVB	suspension polymerization				Cr(VI) at 50 mg L^{-1}	61.35 at pH=2.5, 35 °C, 60 min	[43]
EDA-NMPs	Ethylenediamine-functionalized magnetic	1 g Fe_3O_4 8 mL GMA, 4 mL MMA	GMA and MMA	suspension polymerization and ring-opening reactions				Cr(VI) at 50 mg L^{-1}	136.98 at pH=2.5, 35 °C in 30 min	[44]
DETA-NMPs	diethylenetriamine-functionalized magnetic	1 g Fe_3O_4 8 mL GMA, 4 mL MMA	GMA and MMA	suspension polymerization and ring-opening reactions				Cr(VI) at 50 mg L^{-1}	149.25 at pH=2.5, 35 °C in 30 min	[44]
TETA-NMPs	triethylentetramine -functionalized magnetic	1 g Fe_3O_4 8 mL GMA, 4 mL MMA	GMA and MMA	suspension polymerization and ring-				Cr(VI) at 50 mg L^{-1}	204.08 at pH=2.5, 35 °C in 30 min	[44]

ACCEPTED MANUSCRIPT

				opening reactions						
TEPA-NMPs	tetraethylenepentamine-functionalized magnetic	1 g Fe_3O_4 8 mL GMA, 4 mL MMA	GMA and MMA	suspension polymerization and ring-opening reactions	0.09			Cr(VI) at 50 mg L^{-1}	370.37 at pH=2.5, 35 °C in 30 min	[44]
SH-Fe3O4-NMP	mercapto-functionalized core–shell structured nano-magnetic Fe_3O_4 polymers	5.88% (1 g Fe_3O_4, 8 mL GMA, 4 mL MMA, 0.5 mL DVB)	GMA, MMA and DVB	suspension polymerization and ring-opening reactions				Hg(II) at 100 mg L^{-1}	256.4 at pH=4, 35 °C	[35]
EDA-NMPs	Ethylenediamine-functionalized magnetic	1 g Fe_3O_4 8 mL GMA, 4 mL MMA	GMA and MMA	suspension polymerization and ring-opening reactions				Cu(II) at 10 mg L^{-1}	87.72 at pH=4, 35 °C	[36]
DETA-NMPs	diethylenetriamine-functionalized magnetic	1 g Fe_3O_4 8 mL GMA, 4 mL MMA	GMA and MMA	suspension polymerization and ring-opening reactions				Cu(II) at 10 mg L^{-1}	94.30 at pH=4, 35 °C	[36]
TETA-NMPs	triethylentetramine -functionalized magnetic	1 g Fe_3O_4 8 mL GMA, 4 mL MMA	GMA and MMA	suspension polymerization and ring-opening reactions				Cu(II) at 10 mg L^{-1}	92.60 at pH=4, 35 °C	[36]
TEPA-NMPs	tetraethylenepentamine-	1 g Fe_3O_4 8 mL GMA, 4 mL MMA	GMA, MMA and DVB	suspension polymerization and				Cu(II) at 10 mg L^{-1}	116.80 at pH=4, 35 °C	[36]

ACCEPTED MANUSCRIPT

	functionalized magnetic			ring-opening reactions						
CS-NR-Mag-MIP	core–shell nanoring amino-functionalized superparamagnetic polymer		GMA, MMA and DVB	Coupling grafting reaction with ultrasound-assisted suspension polymerization				BPA at 5–1000 mg L^{-1}	750.2 20 min	[15]
CS-NR-Mag-NIP	core–shell nanoring amino-functionalized magnetic nonimprinted polymer			suspension polymerization and ring-opening reactions				BPA at 5–1000 mg L^{-}	125.0 20 min	[15]
CS-NS-Mag-MIP	Core–shell nanospherescale amino-functionalized magnetic MIP nanoparticles			conventional mechanical agitation (CMA)				BPA at 5–1000 mg L^{-}	275.0 in 60 min	[15]
MGO@MIP	magnetic GO sheet embedded with core–shell MIP microspheres	1:15	GMA and DVB	reflux-precipitation polymerization and surface imprinting method				PCP (10–1000)	789.4 at pH= 4.5, 10 min, 35 °C	[20]
MGO@NIP	magnetic GO sheet embedded with core–shell	1:15	GMA and DVB	reflux-precipitation				PCP (10–1000)	373.2 at pH= 4.5,	[20]

ACCEPTED MANUSCRIPT

	non imprinted polymer microspheres			polymerization and surface imprinting method					60 min, 35 ^{o}C	
T-MMIP hybrid	GO-based ternary magnetic MIP polymer hybrid via *in situ* controllable technique		AM and DVB	*in situ* co-polymerization and subsequent template molecule elution	1015	0.75	4.1	MC	256.3 at pH= 3, 480 min, 70 ^{o}C	[53]
GO-Fe3O4@P	GO-based magnetic polymer	1:50	DVB and GMA	distillation–precipitation polymerization, ring-opening and amidation reactions.	60.41	0.3428		2,4,6-trichlorophenol (2,4,6-TCP) (100 mg/L	232.6 at pH= 5, 10 min, 35 ^{o}C	[47]

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Table 2 Intrinsic physical–chemical and polyelectrolyte properties of chitosan [75, 79].

Physicochemical properties	Polyelectrolyte (at acidic pH)	Biological properties
Linear amino-polysaccharide with high nitrogen content	Cationic biopolymer with high charge density (one positive charge per glucosamine residue)	Biocompatibility (Non-toxic, Biodegradable, Adsorbable)
Numerous reactive groups	Flocculating agent; interacts with negatively charged molecules	Antimicrobial activity (fungi, bacteria, viruses)
Hydrophilic	Filtration and separation	Antiacid, antiulcer, and antitumoral properties
Weak base (powerful nucleophile, pK_a ~6.3)	Entrapment and adsorption propertie; filtration and separation	Blood anticoagulants
Insoluble in water and organic solvents	Film-forming ability	Hypolipidemic activity
Ionic conductivity	Chelating and complexing properties	Bioadhesivity
Rigid D-glucosamine structure	Adhesivity	
High crystallinity	Materials for isolation of biomolecules	

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Capacity to form hydrogen bonds intermolecularly; high viscosity		
Soluble in dilute acidic aqueous solutions		
Chelating and complexing properties		

Table 3 Advantages and limitations of conventional activated carbons, synthetic ion-exchange resins and polymeric absorbents for pollutants removal from solutions

Adsorbent	Advantages	Limitations
Activated carbon (AC)	The most effective adsorbent Very large surface area Porous sorbent High adsorption kinetics and capacity Commercially utilized for dyes and organic pollutants removal High capacity for adsorption of a wide range of contaminants A high-quality treated effluent is obtained (ability to reduce contaminant concentrations to ppm levels)	Expensive The cost increases with the quality The performance depends on the type of carbon used Needs complexing agents for enhanced removal efficiency Poor selective Not suitable for hydrophilic substances Not suitable for vat and disperse dyes High cost of reactivation Poor regeneration due to loss of carbon Inability to reduce contaminant concentrations beyond ppm range
Ion-exchange resin	Hierarchical of pore structure Numerous physicochemical characterization Good surface area Effective sorbent Remarkable selectivity toward aromatic solutes Easy to regenerate without loss of adsorbent	Expensive Sourced from fossil fuel-based raw materials Sensitive to particles The performance depends on the type of resin Not suitable for all dyes Performance depends pH Poor contact with aqueous pollutants Modification is required for improved wetability
Nano-magnetic polymers (NMPs)	High selectivity Low-cost High surface area Small diffusion resistance Remarkable binding capacities for metals, organic pollutants and dyes High number of surface active sites	Susceptible to air oxidation Ease of aggregation in aqueous systems but could be corrected by surface modification. Insufficient magnetic component (the “core”) terminate magnetic

ACCEPTED MANUSCRIPT

	Rapid adsorption kinetics High adsorption efficiency and contaminants removal rate Easy to regenerate (the magnetic properties enable fast and facile solid–liquid separation under an applied magnetic field, without centrifugation or filtration)	response due to disorientation of the surface spin Insufficient polymer component (the ‘‘shell’’) could lead to poor adsorption capacity
Chitosan	Cheap natural polymer Biodegradable Environmentally benign Extremely cost-effective Amphiphilic in nature Ability to form inclusion complexes with organic molecules Outstanding metal and dye-binding capacities High efficiency and selectivity in detoxifying both very dilute or concentrated solutions excellent diffusion properties A high-quality treated effluent is obtained (ability to reduce contaminant concentrations to ppb levels) Versatile sorbent Easy to regenerate due to relatively weak interactions	Nonporous sorbent Extremely low specific area The sorption capacity depends on the precursor, affinity for water, amino group content, crystallinity and the degree of N-acetylation Inconsistency in characteristics of the bead Performance depends pH Requires chemical modification for enhanced performance Low affinity for basic dyes Soluble in acidic media but could be modified to Improve their properties. Not suitable for column setup
Cyclodextrin	Cheap natural polymer Environmentally benign Extremely cost-effective Amphiphilic in nature Ability to form inclusion complexes with organic molecules, especially aromatics Outstanding capacities for binding organic molecule and dye A high-quality treated effluent is obtained Versatile sorbent Easy to regenerate due to relatively weak interactions	Nonporous sorbent (extremely low specific area) Low affinity for metals The sorption capacity depends on nature of the contaminant The inclusion process depends on size of the CD cavity, and size and shape, polarity of pollutants Temperature, ionic strength, and pH-dependence Requires chemical modification for enhanced performance, especially for heavy metal removal
Covalent organic polymers (COPs)	Remarkably high binding affinity for heavy metals High capacity of adsorption equivalent to that of AC despite moderate surface area Faster adsorption kinetics than that of AC Excellent capacity to degrade halogenated organic compounds and dye Remarkable wettability in contaminated solution	Not viable for column setup due to back pressure, which will require a very high energy to overcome for large-scale operation Surface area, not large enough immiscible COPs exhibit low affinity for dyes Not suitable for column setup
Extracellular polymeric substances (EPS)	High molecular weight Play vital roles in common biological wastewater treatments such as membrane bioreactors (MBRs), activated sludge processes and fixed-film processes	Declined P removal efficiency in the presence of high concentration of heavy metals

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

	Provides binding sites for charged particles or molecules as well as metals due to the availability of charged moieties High phosphorus removal efficiency in biological P removal (BPR) systems Play a vital role in developing a stable denitrifying P removal (DPR) system in the presence of heavy metals without affecting the phosphate-accumulating organisms (PAOs), and also protect heavy metals from microbes attack Possess hemiacetal-reducing ends in phenol groups and polysaccharides capable of reducing heavy metals. Ability to prevent or delay toxicants from interacting with microbial cells by chemical reactions and/or mass transfer limitation	

Table 4 Market price of laboratory grade polymeric adsorbents.

Sample	Catalog/Case Number	Manufacturer	Quantity	Price ($)
Chitosan	AAJ6414336	Alfa Aesar™	500 g	189.00
Chitosan	9012-76-4	Aldrich	250 g	201.00
Beta Cyclodextrin	AC406005000	Acros Organics	500 g	154.10
Beta Cyclodextrin	7585-39-9	Aldrich	1 kg	551.00
Magnetite (MP)	50-901-14643	Strem Chemical, Inc	500 g	55.00
Nano Magnetite (NMP)	1317-61-9	Aldrich	250 g	296.00
N,N-diisopropylethylamine Piperazine (both for COP-1)	7087-68-5 110-85-0	Sigma Aldrich Sigma Aldrich	1 L 500 g	419.50 720.00

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

N,N-diisopropylethylamine	367840010	Acros Organics	1 L	332.50
Piperazine (both for COP-1)	AC131295000	Acros Organics	500 g	56.20

ACCEPTED MANUSCRIPT