Synthesis and characterization of molecular imprinted nanomaterials for the removal of heavy metals from water

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ABSTRACT
Heavy metal pollution presents an important global environmental problem due to its toxic effects that may accumulate in the food chain. For removal of toxic heavy metals from different sources of water, various technologies such as chemical precipitation, membrane filtration, solvent extraction, electrodialysis, ion exchange and adsorption are employed. However, only the adsorption method is the most versatile and widely used, while others are more expensive and of low feasibility. A wide variety of porous materials, such as agricultural waste, polymers, clay minerals and carbon materials have been investigated as adsorbents for the removal of toxic metals. In this study, the adsorbent stability in acidic and basic medium, desorption study as well as its reusability and recyclability were adequately assessed. The effect of contact time, pH and adsorbent dose were addressed by various authors, which specifies the reliability and efficiency of nanoparticles as potential adsorbents. The molecular imprinted (MI) nanomaterials are also suitable for a broad spectrum of applications such as biosensing, molecular imaging, and drug delivery. However, there are certain setbacks that can be reduced or diminished through the coating of nanoparticles with various polymers of biological origin. These biopolymers are biocompatible, non-toxic and renewable. They possess chemical groups that permit further functionalization of the MI nanoparticles. Multifunctional entities can be created through decoration with specific molecules e.g. proteins, peptides, drugs, antibodies, cells and transfection agents. Therefore, MI nanomaterials may be used as the future materials for the environment and human sustainability.

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1. Introduction

Water pollution is one of the most serious problems that have been addressed by several water pollution controlling bodies at national and international levels. Water contaminated with toxic metals is considered as a serious environmental problem in human society [1]. Heavy metals in water originate from geological erosion and natural calamities as well as rapid development of human civilization, such as industrialization, urbanization, mining operation, atomic power plants, pharmaceuticals, pesticides, forest fire and tanneries [2]. Heavy metals are elements having atomic weights between 63.55 and 200.59 and a specific gravity greater than 4.0. Living organisms require trace amounts of some heavy metals including Co, Cu, Fe, Mn, Mo, V, Sr, and Zn. They are known as essential metals but their excessive levels can be detrimental to organisms. Heavy metals including Hg, Cr, Cd, As, Pb, Sr, etc. are nonessential metals and considered to be a great threat to aquatic life as well as humans, plants, and other living beings [3]. These heavy metal ions are directly released into the natural water by various industrial and human activities. These metals exist in surface water in colloidal, particulate and dissolved forms, although dissolved concentration is very low and are generally in the form of ions or unionized organometallic chelates or complexes. The solubility of trace metals in surface water is controlled by the water pH and the type of concentration of ligands on which the metal could adsorb such as clay, silica, alumina and organic matter [4–6]. The colloidal and particulate forms of metals are found in hydroxides, oxides, silicates, sulfides that get adsorbed to clay, silica and organic matter. These toxic metals are not only threat to the aquatic organisms but also cause severe health disorders in humans by accumulation through food chain [7]. The toxicity of heavy metals may be caused by the inhibition and reduction of various enzymes, complexation with certain ligands of amino acids and substitution of essential metal ions from enzymes [8].

Nowadays small and large scale industries are discharging their effluents directly into the water sources and thus polluting them with toxic metals. Toxicological studies have found that the degree of toxicity of heavy metals depends on the oxidation state of metal ions [9]. For instance, chromium is a common contaminant in industrial effluent water of electroplating, tanning, paint and pigment production as well as metallurgical industries. It is usually presented in the environment in two stable oxidation states Cr(III) and Cr(VI). It is well known that chromium(III) is considered as an essential micronutrient for human, plant and animal metabolism, while chromium(VI) is soluble and hazardous to health. In natural water chromium ions mainly appear as chromate and cationic hydroxo complexes. The recommended limits for Cr(VI) in drinking water is 0.05 ppm [10]. Copper(II) play a crucial role in the development of bones, central nervous system, and connective tissues. The acceptable limit of Cu in drinking water is 2.0 mg/l [11], but its concentration varies from 0.01 to 0.5 mg/l, which is tolerable and poses no serious health threat to the human and living organism [12]. Cadmium(II) is highly toxic and cause a number of acute and chronic disorders, such as renal damage, emphysema, hypertension and skeletal malformation in the fetus [13–15]. The maximum concentration of Cd in potable water is 0.005 mg/l [16,17]. Arsenic is presented in two forms: organic and inorganic. Inorganic arsenic is a commonly known carcinogen [18]. The maximum acceptable concentration of As in drinking water is 0.01 mg/l [19]. Mercury that deposits onto the earth’s surface from the air can make its way into waterways, where it is converted by microorganisms into the organic compound dimethyl mercury, a highly toxic form of mercury, which has been implicated in causing brain and liver damage [20]. Methyl mercury concentrations increase with food chain levels, i.e., bioaccumulation [21–23]. As a result, consumption of food (mercury-contaminated fish) by humans (pregnant women) causes developmental effects in their offspring such as low intelligence levels, delayed neurodevelopment and subtle changes in vision, memory and language [24]. The maximum acceptable concentration of Hg in drinking water is 0.001 mg/l [25,26]. Lead can enter the human body through water, food and air. Its implication can be seen in the form of kidney damage, miscarriage, brain damage impulsive behavior and hyperactivity. Long-term exposure to lead or its oxides can cause nephropathy [27]. Its concentration in drinking water is 0.01 mg/l [28]. Hence, removal of heavy metals from wastewater and drinking water is of great importance due to their serious health effects [29]. Various technologies such as chemical precipitation, membrane filtration, solvent extraction, electro dialysis, ion exchange and adsorption are applicable for the removal of heavy metals from aqueous solutions [30–34]. Ion exchange usually requires a high capital investment for the equipment as well as high operational cost [35]. However, only the adsorption method is the most versatile and widely used, because the traditional methods are more expensive and least feasible for small-scale industries [36,37]. A wide variety of porous materials, such as agricultural waste, polymers, clay minerals and carbon materials have been investigated as adsorbents for the removal of toxic metals [38]. In recent years, molecular imprinting (MI) adsorbents have been increasingly used in chromatographic separation, catalysis and sensing. But up to our knowledge, limited studies have been carried on to the removal and recovery of heavy metals from waste streams [39,40]. These nanomaterials are very effective as a separation medium for water purification as they have physicochemical properties such as the high surface area to mass ratio due to decreased size and material dimension that leads to the availability of a large number of atoms or molecules on the surface to enhance the adsorption of contaminants [41–43].

2. Mechanism for synthetic process of molecular imprinted nanomaterials

2.1. General principle

Molecular imprinting of synthetic polymers is a process where functional and cross-linking monomers are copolymerized in the presence of the analyte (imprint molecule), which acts as a molecular template [44]. The functional monomers initially form a complex with the imprint molecule, and following polymerization, their functional groups are held in
position by the highly cross-linked polymeric structure. Subsequent removal of the imprint molecule reveals binding sites that are complementary in size and shape to the analyte. In that way, a molecular memory is introduced into the polymer, which is now capable of rebinding the analyte with a very high specificity. There are two distinct approaches to MI as shown in Fig. 1 [45]. A polymerization complex between imprint molecule and functional monomers can be formed via non-covalent interactions (self-assembly). Alternatively, monomers can be covalently coupled to the imprint molecule, that is, a polymerizable derivative of the imprint molecule is synthesized. Owing to the greater stability of covalent bonds, covalent imprinting protocols should conceivably yield a more homogeneous population of binding sites, and indeed, there have been reports suggesting that this might be the case [46]. Moreover, the yield in binding sites is relative to the amount of imprint molecule used that should be higher than noncovalent protocols. This approach has been developed primarily by Wulff and co-workers [47]. On the other hand, the non-covalent imprinting approach, which has been pioneered by Mosbach and co-workers, is more flexible concerning the choice of functional monomers, possible target molecules, and the use of the imprinted nanomaterials [48]. The distinct approach of molecular imprinting (as in Fig. 2) “the synthesis route for Silica coated magnetite (Fe₃O₄@SiO₂) nanoparticles”.

The aim of the present review works was to study the MI nanomaterials and its application for the removal of heavy metals from aqueous solution under the influence of various operational parameters such as the effect of concentration, contact time, adsorbent dose and solution pH. It was reported by various research papers that the experimental data were fitted to the Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) adsorption isotherms [49]. In order to understand the rate and mechanism of the adsorption process, the adsorption...
kinetics was also carried with its relation to adsorption mechanism. The thermodynamic analysis was also reviewed to elucidate the adsorption and desorption mechanism of heavy metals [50]. Therefore, MI nanoparticles may be the future materials for the removal of heavy metals from wastewater.

2.2. Methods for preparing nanomaterials

Several chemical methods can be used to synthesize MI nanoparticles for different applications such as co-precipitation, reverse micelles, sol–gel synthesis, hydrothermal reactions, thermolysis of precursors, flow injection syntheses, and electrospray syntheses [51]. The synthesis of MI nanoparticles is a complex process because of their colloidal nature. For metal removal applications, an adequate surface modification of the nanoparticles is a critical aspect regarding both selectivity and aqueous stability of these materials.

A brief description of the most widely used methods for preparing nanomaterials with applications in metals removal is discussed below.

2.2.1. Co-precipitation method

It is one of the most common chemical wet methods for obtaining MI nanoparticles. This method consists of two parts, firstly mixing ferric and ferrous ions in a 1:2 molar ratio in basic solutions with pH ranging from 9 to 12 at room temperature or at elevated temperature. Then prepare Fe3O4 suspension in ethanol medium as a core by adding a 2–3 mL solution of 5% polyvinyl alcohol (PVA) as an adhesive; on which easily bind-up the SiO2 by adding the sodium silicate (Na2SiO3) solution in a molar ratio 1:1. The size and shape of the Fe3O4@SiO2 nanoparticles depends on the type of salt used such as chlorides, sulfates, nitrates, perchlorates, etc., the ferric and ferrous ions ratio, the reaction temperature, the PH value, ionic strength of the medium, and other reaction parameters, e.g., stirring rate, dropping speed of basic solution [52,53].

2.2.2. Reverse micellar method

Microemulsion is a thermodynamically stable isotropic dispersion of two immiscible phases (water and oil) in the presence of surfactant, the surfactant molecules may form a monolayer at the interface between the oil and water phases, with the hydrophobic tails of the surfactant molecules dissolved in the oil phase and the hydrophilic head groups in the aqueous phase [54]. Particularly, water-in-oil (w/o) microemulsions are synthesized by well-defined nanodroplets of the aqueous phase, dispersed by the assembly of surfactant molecules in a continuous oil phase.

Vidal-Vidal et al. [55] have reported the synthesis of monodisperse maghemite NPs by the one pot microemulsion method. Chin and Yaacob reported the synthesis of magnetic iron oxide NPs (<10 nm) via water in oil (w/o) microemulsion [56]. When it was compared to the particles produced by Massart's procedure, it was found that particles produced by microemulsion technique were smaller in size and were higher in saturation magnetization [57].

2.2.3. Hydrothermal method

Hydrothermal syntheses of Fe3O4@TiO2 nanoparticles have been reported in the literature during the last decade and have been widely used in the synthesis of core–shell nanoparticles [58]. In this method, reactions are performed in aqueous media in reactors or autoclaves, where pressure is kept higher than 2000 psi and the temperature is above 200 °C. There are two main routes for the formation of magnetite nanomaterials via hydrothermal conditions: hydrolysis and oxidation or neutralization of mixed metal hydroxides. These two reactions are very similar to each other. In this process, the reaction parameters such as solvent, temperature and time usually have important effects on the products. In the hydrothermal process, the particle size is controlled by the rate processes of nucleation and grain growth [59].

2.2.4. Thermal decomposition method

Thermal decomposition of organic compounds in suitable solvents has been widely used in the synthesis of magnetite nanoparticles. Decomposition of Fe(cup)3 (cup = N-nitrosophenylhydroxyl amine), Fe(AC)3 (AC = acetylacetonate), or Fe(CO)5 and followed by oxidation yields a high-quality monodispersed iron oxide NPs. Many researchers [60–64] have reported a general decomposition approach for the synthesis of size-controlled monodispersed magnetite NPs at high temperature (265 °C) by decomposition of Fe(AC)3 in phenyl ether in the presence of alcohol, oleic acid and oleyl amine. The as-synthesized Fe3O4 nanoparticles are easily converted into YFe2O3 NPs by annealing at high temperature (250 °C) and oxygen for 2h. Generally, direct decomposition of Fe(Cup)3 single precursor produces monodispersed YFe2O3 nanoparticles [65].

2.2.5. Sol–gel method

The sol–gel technique is the most common method of synthesizing silica nano-particles. It involves the simultaneous hydrolysis and condensation reaction of the metal alkoxide [66]. However, the physical properties of nanosized spherical colloidal silica, prepared from tetraethylorthosilicate (TEOS) in ethanol are difficult to reproduce. They often depend on the method of isolation of the product [67,68]. Kolbe in 1956 observed the formation of silica particles by reacting TEOS in alkali solution with water in the presence of certain bases [69]. A typical sol–gel reaction is hydrolysis and condensation of TEOS as a precursor of silica. Both reactions are concurrent and reversible depending on the reaction conditions such as pH and temperature [70–73].

There have been abundant researches related to the functionalization of MI nanoparticles with metal oxides and metal sulfides because of its importance of its unique physical and chemical properties. In general, researchers concentrate on using ZnO, MgO, CaO, SnO2, and Al2O3 for the functionalization of magnetite nanoparticles [74]. Among magnetic materials iron oxides, CoO, NiO and CoFe2O4 are the most commonly used [75]. For optical and electrical functional materials TiO2, ZnS and Y2O3 are used for the functionalization of magnetite nanoparticles [76]. For example, the synthesis route for TiO2 coated magnetite nanoparticles as shown in Fig. 3.
3. Applications for the removal of heavy metals from aqueous solution

A brief description of the most widely used applications for the removal of heavy metals from aqueous solution is discussed below.

3.1. Adsorption process

In order to understand the rate and mechanism of the adsorption process, the adsorption kinetics were also reported with its relation to adsorption mechanism by various researchers [77-79]. Adsorption isotherm was carried by stirring fixed amount of nanocomposite as a nano sorbent (g) with a solution of a metal salt for 15 min at room temperature to attain equilibrium [80]. The concentration of unadsorbed metal ions was found out with the help of calibration graph of the metal solution at a fixed wavelength with varying initial metal concentration. After the equilibration the pH of the reaction medium was changed prior to finding out the metal concentration of the filtrate, pH should be stabilized to 6–7 [81]. The amount of adsorbed metal (C_a) was then found out by applying the formula:

\[ C_a = C_i - C_f \]

where \( C_i \) = initial concentration, \( C_f \) = final concentration.

Percentage recovery factor (%R) was calculated by the following equation:

\[ %R = \frac{C_a}{C_o} \times 100 \]

where \( C_a \) and \( C_o \) are adsorbed and initial concentration of metal ions.

The absorption measured at a fixed wavelength (\( \lambda_{\text{max}} \)) by diluting the concentration of the standard solution in a fixed ratio, is plotted in the graph [82]. The concentration of adsorbed metal ions was calculated as a difference between the initial concentration of the solution and the final concentration after the equilibration. A number of metal ions adsorbed at time t, \( q_t \) in mg/g were calculated as a mass balance equation:

\[ q_t = \frac{(C_o - C_f) \times V}{m} \]

where \( C_o \), \( C_f \), \( V \), \( m \) are initial concentration of metal ions, the concentration of metal ions after time t, the volume of the solution and mass of the adsorbent respectively. It was reported by various researchers that the observed experimental data of adsorption would fit into different adsorption isotherms such as Langmuir and Freundlich [83].

3.2. Effect of adsorbent dose, pH and time intervals

It was pragmatic that in order to study the effect of adsorbent dosage on the adsorption capacity, different metal solutions were taken and pH of the solutions was adjusted accordingly. Then various amounts of adsorbents were added to the solutions at room temperature for stirring 15–20 min [84]. The effect of pH on adsorption capacity (surface adsorption phenomenon) of metal ions (Cu^{2+}) was considered at room temperature by varying pH of the reaction medium 2–10 while keeping other parameters constant [85]. After the reaction, the concentration of metal ions (Cu^{2+}) was calculated with the help of UV–vis spectrophotometer [86]. To study the effect of time on adsorption capacity, the adsorbent was mixed with metal ion solutions at room temperature for various time intervals ranging from 5 to 25 min as reported by various authors [87].

3.3. Desorption and regeneration study

In order to understand the mechanism of the regeneration cycle and its relation to desorption process researchers have shared their views, which specifies that the desorption of heavy metal ions, in the beginning, was found to be maximum, but later on, desorption capacity was decreased with increasing number of regeneration cycle [88]. Desorption study was carried out by using acidic solution (HCl) as an eluent for eluting the adsorbed metal ions from the adsorbent. Then nano sorbent was separated by applying external magnetic field and the concentration of eluted metal ions in the filtrate was measured with the help of calibration graph of metal ions (Cu^{2+})
Fig. 4 – SEM images of silica coated magnetite (Fe$_3$O$_4$@SiO$_2$) nanoparticles before adsorption (a) and after adsorbed metal ions on the surface of nanoparticles (b).

by measuring the absorbance using UV–visible spectrophotometer. It was reported that the desorption of heavy metal ions, in the beginning, could be almost 92–95%. Although the desorption capacity was decreased with increasing number of regeneration cycle but remained adequate till more cycles were assessed [89].

4. Novel properties of MI nanomaterials

Currently, MI nanoparticles with novel properties and functions have been widely studied in the field of separation technologies due to its cost-effective synthesis, easy coating or surface modification and ability to control materials on nanoscale dimensions. These provide amazing versatility in separation techniques [90,91]. Apart from these, low toxicity, chemical inertness and biocompatibility of Fe$_3$O$_4$@SiO$_2$ nanoparticles show the potential in biomedical application [92,93].

4.1. Nano size and large surface area

When materials size becomes 1–100 nm in range, it shows a drastic change in their properties associated with the large area to volume ratio (Fig. 4) [94]. As the surface of the materials increased there would be more reactive sites for reactions to occur [95–97]. This concept of nanotechnology is utilizing these unique properties in the day to day applications.

4.2. Magnetic properties

Magnetic properties have been found to appear in small ferromagnetic or ferrimagnetic nanoparticles (2–20 nm) as investigated by researchers [98]. It was observed that in sufficiently small nanoparticles, magnetization can randomly flip direction under the influence of temperature [99]. Paramagnetism occurs in nanoparticles composed of a single magnetic domain with diameter 3–50 nm, depending on the nanomaterials. Normally ferromagnetic or ferrimagnetic materials undergo a transition to a paramagnetic state above its curie temperature while superparamagnetism is different from this standard transition since it occurs below the Curie temperature of the material [100,101]. When an external magnetic field is applied to an assembly of superparamagnetic nanoparticles, their magnetic moments tend to align along the applied field, leading to a net magnetization. The magnetization curve of the assembly shows magnetization as a function of the applied field, that is a reversible S-shaped as shown in Fig. 5 [102–104].

4.3. Surface modifiability

MI nanoparticles have hydrophobic surfaces with a large surface area to volume ratio that causes hydrophobic interactions between the nanoparticles that lead to the coagulation or agglomeration of nanoparticles [105,106]. Agglomeration of nanoparticles forms large clusters resulting in increased particle size. It has been observed that the surface of the magnetite nanoparticles can be easily modified by inorganic and organic moieties due to the exposed hydroxyl group on their surfaces [107,108]. Modified surface also provides a better prospect for further functionalization apart from providing a stable colloidal solution, better dispersion and protective layer to avoid atmospheric interference as shown in Fig. 6 [109].

4.4. Biocompatibility

MI nanoparticles and its composites have been widely used in applied medicine to develop therapeutic methods of the
endogenous intoxication syndrome to create a new class of biocompatible sorbents [110]. MI nanomaterials in particular have been thoroughly investigated as novel magnetic resonance imaging [111], contrast agents [112], targeted delivery of drugs or genes [113], tissue engineering [114], targeted destruction of tumor tissue through hyperthermia [115], magnetic transfections [116], iron detection [117], chelation therapy [118,119] and tissue engineering [120] due to a combination of favorable superparamagnetic properties, biodegradability, and easy modification of surface properties for improved in vivo kinetics and multifunctionality [121,122].

5. Organic compound coating on the surface of the MI nanomaterials

Organic compounds are often employed to passivate the surface of the MI nanomaterials during or after preparing procedure to avoid agglomeration, to enhance their application in the environmental and biological fields [123-127]. Various researches have been conducted to synthesize organic micro and macromolecules functionalized core-shell nanoparticles with corresponding properties [128-136]. Amphiphilic type refers to the surface of functionalized core–shell nanoparticles containing both hydrophilic and hydrophobic chemical groups [137,138]. The main chain of these functionalized surfactants showed concurrence of hydrophobic and hydrophilic structural regions, which make the functionalized nanoparticles, possess both oil-solubility and water-solubility such as sulfuric lysine [139-141]. Researchers have synthesized the core–shell nanoparticles coated with various long chain fatty acids such as phosphate and phosphonates [142-152]. Which shows the coating of alkyl phosphate and phosphonate were valuable to get thermodynamically stable dispersion of core–shell nanoparticles [153,154]. The different organic functional groups attached to the surface of core-shell nanoparticles are shown in Fig. 7.

5.1. Biological molecules

Various biological molecules such as proteins [155,156], polypeptides [157], antibodies [158,159], biotin [160,161] and avidin [162,163], etc. [164-167] may bound to the surface of core–shell nanoparticles directly or indirectly by chemically coupling via some functional end groups to make the nanoparticles target specific [168,169]. The biological molecules functionalized Fe3O4@SiO2 nanoparticles will greatly improve the particle biocompatibility [170-176]. Such core–shell nanoparticles can be very useful to assist in an
effective separation of proteins [177,178], DNA [179–181], cells [182–184], antibodies [185], peptides [186], drugs [187], biochemical products [188], transfection agents [162] and other ligands [189]. The graphical illustration of the structure of multifunctional core–shell nanoparticles with different types of the magnetic core is shown in Fig. 8 [190–192].

6. Conclusions

The outcome of the study will be an addition in the utilization of MI nanomaterials with high imprinting coefficients and retention capacity offers a possible application for removal of heavy metals from aqueous solution. Simple preparation procedures and significant selectivity of these nanomaterials, arising out of imprinting open up a novel method for the treatment of polluted effluents. It was pragmatic that adsorption was pH dependent and adsorption mechanism shows an ion exchange as well as electrostatic binding. Desorption investigates that acidic solution was an efficient eluent with 95% of heavy metal ions released by the nanosorbent from the regeneration cycle. These nanoparticles also have tremendous potential in the field of biomedical applications, on account of their similar size to biological molecules. In particular, MI nanoparticles can be synthesized in such a way as to possess unique superparamagnetic properties to be biocompatible and to remain inert with respect to cells and molecules of interest. A silica coating on the surface of nanoparticles decreases the aggregation, oxidation and toxicity of these materials. The shielding of magnetic dipole interaction and enhancement of repulsion due to negatively charged silica coating stabilizes the magnetic nanoparticles. Hence, MI nanomaterials create a new class of biocompatible sorbents, which can be widely used in applied medicine to develop therapeutic methods for disease and pollution control. In addition to this, these sorbents properties recycled in the environment for remediation of heavy metals on a worldwide scale.

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