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Use of iron oxide magnetic nanosorbents for Cr (VI) removal from aqueous solutions: A review

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Abstract
This review paper focuses on the use of iron oxide nanosorbents for the removal of hexavalent Chromium [Cr(VI)], from aqueous media. Cr(VI) is a well-known toxic heavy metal, which can cause severe damages to the human health even with the presence of trace levels. Chromium continuously enters into water streams from different sources. Several methods are available for Cr(VI) removal and some of them are well established in industrial scale whilst some are still in laboratory scale. Reduction followed by chemical precipitation, adsorption, electro-kinetic remediation, membrane separation processes and bioremediation are some of the removal techniques. Each method is associated with both advantages and disadvantages. Currently, the use of nanosorbents for the aqueous chromium removal is popular among researchers and iron oxide nanoparticles are the most frequently used nanosorbents. This review paper summarizes the performance of different iron oxide nanosorbents studied on the last decade. The direct comparison of these results is difficult due to different experimental conditions used in each study. Adsorption isotherms and adsorption kinetics models are also discussed in this review paper. The effect of solution pH, temperature, initial Cr(VI) concentration, adsorbent dosage and other coexisting ions are also briefly discussed. From the results it is evident that, more attention needs to be paid on the industrial application of the technologies which were successful in the laboratory scale.

Key words: Adsorption, Adsorption capacity, Chromium, Iron oxide nanoparticles, Nanosorbents

I. Introduction

Nowadays, there is a continuously increasing worldwide concern for the development of wastewater treatment technologies. Great attention has been paid to the effective removal of heavy metal ions, especially highly toxic heavy metals such as chromium[1-3], cadmium[4, 5], mercury[6, 7], arsenic[8, 9] and lead[10, 11] from the environment. Different treatment technologies are available for the removal of toxic heavy metals. The adsorption [12], chemical precipitation [13], ion exchange [14], coagulation [11], reverse osmosis [9], electrolysis and membrane process [15] are widely used. However, among all these methods, adsorption is considered as one of the most effective, efficient and economical method for the removal of pollutants from wastewater [16, 17]. The utilization of iron oxide nanomaterials as the adsorbents has been received much attention due to their unique properties, such as high surface area-to-volume ratio, surface modifiability, excellent magnetic properties, great biocompatibility, ease of separation using external magnetic field, reusability and comparatively low cost [18, 19].

I.1 Chromium

Chromium is widely used in many industrial processes such as mining industry, metallurgical industry (steel, ferrous- and nonferrous alloys), refractories (chrome and chrome-magnetite), electroplating, tannery, timber treatment and some other chemical industries [20, 21]. Leakage, unsuitable storage and/or improper disposal practices are the main reasons for releasing the considerable quantities of chromium to the environment. Chromite and other chromium bearing minerals present in bedrock and soil releases natural chromium to the environment with the time. It was reported that, the world wide annual discharge of chromium into the environment from industrial and manufacturing activities is nearly 170,000 tons[22]. The maximum level of total chromium level in drinking water is set as 0.05 mg/L, by World Health Organization (WHO)[23].

Chromium occurs in several oxidation states ranging from -2 to +6. However, only trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) are predominant in the environment. In the natural environment, Cr(III) is most immobile, less soluble and stable, whereas Cr(VI) is highly mobile, soluble and bioavailable [20]. Major Cr(VI) species include, $HCrO_4^-$,chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$

). Cr(III) is the dominant form of Chromium at low pH (<4) [24]. Cr(III) is biologically important (50–200 μg day^{-1}) to the human body, in which it influences sugar and lipid metabolism in humans. On the other hand, hexavalent chromium (Cr(VI)) is highly toxic, teratogenic and mutagenic [25]. It can cause severe damages to the human health including, but not limited to, liver and kidney damage, producing lung tumours, severe diarrhoea, allergic dermatitis, skin irritation, internal haemorrhage and respiratory problems [26-28].

Since Cr(VI) causes a great threat to humans as well as animals, cleaning up this contaminant from soil and water is critical [20].Several methods are available for the decontamination of waters contaminated with Cr(VI) compounds. Some of these methods are reduction followed by chemical precipitation[2], adsorption, electro-kinetic remediation, membrane separation processes[29] and biosorption [30]. In the presence of electron donors, Cr(VI) can be reduced to Cr(III), which is less toxic. Iron(II), reduced sulphur and organic matter are chief sources of electrons to reduce Cr(VI). The species distribution of chromium in aqueous solution in different pH values are illustrated in the Fig 1, derived from [31].

I.2 Magnetic Nanoparticles (MNPs)

The nanoparticles (NPs) are ultrafine particles in the size of nanometre order. In many cases, the particles from 1 to 100 nm are generally called as nanoparticles. The nanosized magnetic materials show many novel properties, especially, magnetisation behaviour different than bulk magnetic material [32, 33]. Recently, the use of nanosized magnetic material as adsorbents has attracted increasing interest due to their high surface area and unique superparamagnetism [28, 34]. These properties lead to high adsorption efficiency, high removal rate of contaminants and easy and rapid separation of adsorbent from solution using magnetic field. The magnetic nanoparticles are reusable after magnetic separation, by removing the adsorbed toxic contaminants [35].

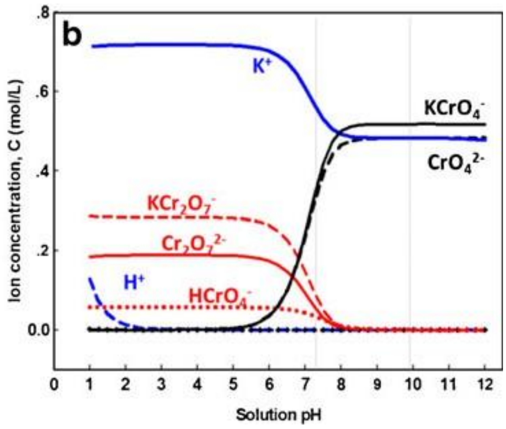

Fig 1:Cr(VI) species distribution in different pH

Currently magnetic nanoparticles are used in wide range of applications, including shape-selective catalysis [36], chromatographic separations [37], sorption of metal ions, enzyme encapsulation, in fields of biotechnology and biomedicine for applications such as cell labelling and separation [38], magnetic resonance imaging (MRI) [39], enzyme and protein separations [40], targeted drug delivery [41] and magnetic ferrous fluids hyperthermia [42]. To date, many technologies, mainly co-precipitation [43, 44], microemulsion[45], thermal decomposition [46], hydrothermal synthesis [47],microwave assisted [48], sol-gel [49] and sonochemicalsynthesis[50] have been applied and reviewed for the production of these magnetic nanoparticles.

The stability of magnetic nanoparticles is utmost important for their applications. This can be greatly improved by preventing their oxidation and aggregation. Modification of the surface of magnetic nanoparticles by attaching organic and/or inorganic materials is proven to be greatly enhances the stability and prevents aggregation. Further these attached groups providespecific functionalities that can be selective for ion uptake [51]. Surface functionalization can be done with organic materials Such as amino groups, carboxyl acid, citric acid, oleic acid, silane, natural polymers (dextran, starch, chitosan, etc.), synthetic polymers (PVA, PAA, alginate, etc.) and inorganic materials such as silica, gold, silver, platinum, palladium, iron, carbon, metal oxides/metal sulphides [52].

Regeneration of the magnetic nanoparticles has been studied in some published works. As the adsorption of heavy metals on to iron oxide nanosorbents is highly pH dependant, the used nanosorbents can be regenerated simply by changing the solution pH. In many cases metal removal capacity of the adsorbent is well maintained after several number of adsorption-desorption cycles [53-56]. The adsorption mechanism has direct impact on feasibility of regeneration of magnetic nanoparticle. As an example in some cases chemical adsorption (chemical bond formation) of Fe_3O_4can limit the regeneration[57], but this can be overcome by surface modification/coating to prevent the magnetic core from chemical adsorption and redox reaction [58].

Among the magnetic nanosized materials, iron oxides play a major role in many areas of chemistry, physics and materials science. Iron oxides exist in many forms in nature where, magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), hematite (α-Fe_2O_3) and goethite (α-FeOOH) being probably the most common. In particular, magnetite and maghemite have been investigated extensively for environmental and bio-application. In addition to convenient magnetic properties, low toxicity and price, the iron oxide nanoparticles exhibit high surface to volume ratios. Their ability for surface chemical modification can show enhanced capacity for heavy metal uptake in water treatment procedures.

II. Use of Iron oxide nanosorbents for aqueous Cr(VI) removal

Currently, there is a fast growing interest in using iron oxide nanomaterials for heavy metal removal. Several studies have been conducted for aqueous hexavalent chromium removal and adsorption capacities of some of the nanosorbents are presented in the Table 1. Magnetite NPs, maghemite NPs and mixtures of above two NPs were extensively studiedfor Cr(VI) removal. Hu, Chen [53] studied the performance and mechanism of different heavy metals (Cr(VI), Cu(II), and Ni(II)) removal form industrial wastewater, using maghemite nanoparticles. Adsorption equilibrium was achieved within 10 minutes for all three heavy metals and at equilibrium, adsorption capacity of NPs for Cr(VI) was reported as 17.43 mg/g at pH 2.5. The adsorption mechanism was identified as electrostatic attraction and ion exchange. In another study, 19.2 mg/g adsorption capacity was reported at pH 2.5 and equilibrium was reached at 15 minutes, which is comparatively fast. Effect of coexisting ions such as Na^+, Ca^{2+}, Mg^{2+},Cu^{2+}, Ni^{2+}, NO_3^- , and Cl^- was ignorable [56].

Magnetite nanoparticles with or without functionalization agents have also been widely studied for aqueous Cr(VI) removal. Shen, Pan [59]was done a study to remove Cr(VI) from copper and chromium co-existing water system, with amino functionalized nanosized magnetite particles and found that adsorption of Cu(II) and Cr(VI) on amino functionalized MNPs was competitive as well as cooperative. Maximum Cr(VI) uptake was reported as 370.37 mg/g. In a different study, diatomite supported and unsupported magnetite nanoparticles was prepared and this nanocomposite was used as the adsorbent for Cr(VI).The diatomite supported magnetite revealed a better adsorption capacity than the unsupported magnetite [57]. Poly acrylic acid (PAA) coated magnetite nanoparticles followed by amino functionalization revealed adsorption capacity of 11.24 mg/g for Cr(VI) [60]. The montmorillonite-supported and unsupported magnetite were also used for the removal of hexavalent chromium and adsorption capacities for unsupported magnetite and supported were 10.6 mg/g and 15.3 mg/g, respectively [61].

Arsenic and chromium removal by mixed magnetite and maghemite nanoparticles was investigated and the maximum adsorption of chromium was found as 2.4 mg/g at pH 2 with an initial Cr(VI) concentration of 1 mg/L. Further it was noted that, arsenic and chromium uptake decreased with increasing phosphate concentration and arsenic removal is more favourable than chromium removal with magnetite-maghemite nanoparticles [62]. In another study, ionically modified (Phosphonium silane coated) iron oxide nanoparticles were used to remove arsenic and chromium. The maximum removal percentage of As(V) and Cr(VI) ions for this adsorbent was 97% (50.5 mg/g) and 67.8% (35.2 mg/g) respectively, at pH 3 and initial concentration of 100 mg/l. In addition to above mentioned nanosorbents, Fe_3O_4/carbon nanotube NPs[31], Fe_3O_4@n-SiO2 NPs[63], ethylenediamine modified Fe_3O_4 NPs [64], polymer-coated Fe_3O_4 NPs [28] and MnO_2/Fe_3O_4/o-MWCNTs [54] were also reported where adsorption capacity ranging from 2.3 mg/g to 186.9 mg/g.

Table 1: Some iron oxide nanosorbents used for Cr(VI) removal

Nanosrbent	**pH**	**Adsorption capacity (mg/g)**	**Reference**
3-Mercaptopropionic acid (3-MPA) functionalized iron oxide NPs	1	45	[65]
Diatomite-supported magnetite NPs	2-2.5	11.4	[57]
Ethylenediamine modified Fe_3O_4 NPs	2	81.5	[64]
Fe_3O_4 (PAA coated and amino functionalized))	2	11.24	[66]
Fe_3O_4 (PAA coated and amino functionalized)	2	370	[59]
Fe_3O_4@n-SiO2 NPs	2	3.78	[63]
Feroxyhyte-coated maghemite NPs	2.5	25.8	[67]

Hematite NPs	3	200	[68]
Iron oxide NPs embedded in orange peel pith	1	5.37	[69]
Maghemite NPs	2.5	17	[53]
Maghemite NPs	2.5	19.2	[56]
Maghemite NPs	4	1.62	[70]
Magnetic Fe_3O_4/CNT NPs (at 20 ^{0}C)	2	47.98	[31]
Magnetic Fe_3O_4/CNT NPs (at 80 ^{0}C)	2	83.54	[31]
Magnetite NPs	4	1.208 ±0.044	[71]
Mesoporous iron–iron oxide nanocomposite	6	34.1	[72]
Mixed magnetite and maghemite	2	2.4	[62]
MnO_2/ Fe_3O_4/o-MWCNTs	2	186.9	[54]
Montmorillonite-supported magnetite NPs	2-2.6	15.3	[61]
Phosphonium-coated MNPs	3	35.2	[55]
Polypyrrole/ Fe_3O_4nanocomposite	2	230.17	[73]
γ-Fe_2O_3@Fe_3O_4	2-3	83.33	[74]

2.1 Factors affecting the Cr(VI) adsorption onto nanomaterial

Several factors can be affected to the adsorption process, such as solution pH, temperature, initial Cr(VI) concentration, adsorbent dosage and presence of other co-existing ions. In addition to these factors, the nanoparticle size and shape also affect to the adsorption performance [75].Higher adsorption capacities can be obtained by optimizing above parameters. The effect of some of these factors are discussed below.

II.1.1 Effect of solution pH

The pH of the solution is an important parameter which controls the adsorption process. It influences the ionization of the adsorptive molecule and hence the surface charge of the adsorbent. Therefore investigating the effect of pH on the adsorption is essential in adsorption experiments. In this particular case, the solution pH can change the surface charge of the adsorbent as well as different ionic forms in chromium. Zeta potential indicates the nature of the electrostatic potential near the surface of a particle. The pH value at which the surface pH is zero, is called the point of zero charge (pH_{pzc}) and is generally used to define or quantify the electrokinetic properties of the surface. Typically the Cr(VI) adsorption on to different iron oxide nanosorbents is favoured at $pH<pH_{pzc}$,as surface of the adsorbent is positively charged [76].It is evident that, the optimum pH for adsorption of Cr(VI) onto different nanosorbents are within 2-3 range. This can be attributed to the presence of Cr(VI) in different ionic forms in the solution at different pH values. $HCrO_4^-$ is the predominant species at pH 2-3 range and it is easily adsorbed due to the low adsorption free energy [57]. On the other hand, a dramatic decrease in adsorption was observed in most cases when increasing the pH value [31, 63]. This may be attributed to few reasons, mainly, the competition with hydroxyl ions for the adsorbent sites and the change of surface charge of the adsorbent leading to electrostatic repulsion between adsorbent and Cr(VI) anions leading to release already adsorbed ions [68].

II.1.2 Effect of temperature

The temperature is also one of the important factors which influence the adsorption of heavy metals on to nanosorbents. Srivastava and Sharma [63] investigated the effect of temperature on Cr(VI) removal using Fe_3O_4@n-SiO2 NPs by increasing the temperature from 25 to 45 ^{0}C and keeping all the other experimental conditions constant and 2% increase in percentage of removal was observed. In another study it was observed that adsorption capacity was increased from 150.8 mg/g to 186.9 mg/g, when increasing the temperature from 2 to 62 ^{0}C, suggesting the endothermic nature of the adsorption process [54]. It is also reported that increase of adsorption capacity from 47.98 mg/g to 83.54 mg/g for 20 and 80 ^{0}C, respectively, when using Fe_3O_4/CNT , as the adsorbent [31].

II.1.3 Effect of initial contaminant concentration

This is a main parameter which can directly affect to the adsorption capacity of an adsorbent. This factor must be taking into consideration when comparing the adsorption capacities of different adsorbents. According to Adegoke, AmooAdekola [68], the amount of Cr (VI) ions adsorbed onto the hematite nanoparticles having different morphologies, increased with increasing Cr(VI) concentration. In another study, it was reported that, by increasing the initial Cr(VI) concentration from 1.36×10^{-2} to 2.4×10^{-2}mol/l, the percentage of removal decreased from 97 ± 0.08 to 95 ± 0.08 %. This may be due to the fact that, lack of available adsorbent sites at higher concentrations, and hence, the percentageadsorption of Cr(VI) decreases [63]. It should be carefully noted that, the actual amount of Cr(VI) adsorbed per unit mass of adsorbent increased with the increase of initial concentration as the two terms “percentage of removal” and “actual amount of removal” are sometimes leading to confusions.

II.1.4 Effect of adsorbent dosage

The Adsorbent dosage is another significant parameter in the examination of the adsorption capacity of an adsorbent. Generally, the percentage of contaminant removal increases with the increase of adsorbent dosage. This may be due to the availability of adsorption sites which adsorbate can get attached. The determination of effect of adsorbent dosage gives an idea about the minimum amount of adsorbent need to be used for adsorption process. This value is useful in the viewpoint of cost. Jiang, Pelaez [70] observed that, the increase of maghemite NP dosage from 0.1 to 1.5 g/L the concentration of Cr(VI) in the aqueous phase was effectively reduced to 100 ppb (initial Cr(VI) concentration 500 ppb) within 60 min.

II.1.5 Effect of other co-existing ions

The presence of different ions in the same solution can be negatively affected to the adsorption efficiency of Cr(VI) onto nanosorbents. The investigation of the effect of coexisting ions is utmost important in adsorption studies as the actual industrial waste water consists of different anions and cations and hence rather complex. There can be a competition between the different ions for same adsorption sites. Hu, Chen [56] investigated the competitive influence ofcommonly coexisting anions (NO_3^- and Cl^-) and cations (Na^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, and Ni^{2+}) with Cr(VI)in chrome-plating wastewater at pH 2.5. It was observed that, the effect of the studied cations are insignificant as they do not have any competition for the adsorption sites of maghemite NPs at this pH and the two anions are biologically inert. The influence of commonly coexisting anions (Cl^-, NO_3^- , SO_4^{2-} and $H_2PO_4^-$) on the overall adsorption of Cr(VI) onto phosphonium silane coated magnetite NPs was studied. It was reported that phosphate anions were able to dramatically reduce the adsorption efficiency. On the other hand the effect of other three anions was insignificant [55]. Similar results for the effect of phosphate ions reported in other works as well [62].

II.2 Adsorption isotherm models

Adsorption isotherm gives the explanation on how adsorbent and adsorbate interact with each other and thereforevital in optimising the use of adsorbents. Various adsorption isotherm models available to describe the equilibrium of adsorption, including Langmuir, Freundlich, BET, Toth, Tempkin, Redlich–Peterson, Sips, Frumkin, Harkins–Jura, Halsey, Henderson and Dubinin–Radushkevich isotherms [77]. According to the majority of reviewed papers, Langmuir and Freundlich isotherm models are best fitted models for Cr(VI) adsorption onto iron oxide nanosorbents [53, 55, 74]and are briefly explained below.

II.2.1 Langmuir adsorption isotherm model

Langmuir adsorption isotherm model assumes monolayer adsorption and adsorption takes place at specific homogeneous sites within the adsorbent. All the sites are considered as identical and energetically equivalent, once aadsorbate molecule occupies a site, no further adsorption can take place in the same site [26, 77]. The Langmuir equation can be expressed as follows:

Non-linear equation;

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (1)$$

Linear equation;

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_a q_e} \quad (2)$$

Where, $q_e$is the amount of adsorbate (chromium) adsorbed at the time of equilibrium in mg/g, $C_e$is the equilibrium concentration of adsorbate in the solution in mg/L, $q_m$is the maximum adsorption capacity in mg/g and $K_a$is the Langmuir isotherm constant in L/mg.

II.2.2 Freundlich adsorption isotherm model

Freundlich isotherm model reflects the multilayer adsorption and applicable for heterogeneous adsorption surfaces. This model assumes that (i) several layers of adsorbate can be attached on the adsorbent and adsorbate will continuously keep binding to the adsorbent and (ii) the energy required for adsorption is not constant, but it varies and exponentially distributed. This model can be represented by below equations.

Non-linear equation;

$$q_e = K_f C_e^{\frac{1}{n}} \quad (3)$$

Linear equation;

$$log q_e = log K_f + \frac{1}{n}(\log C_e) \quad (4)$$

Where $q_e$is the amount of adsorbate at equilibrium time in mg/g, $C_e$is the equilibrium concentration of adsorbate in the solution in mg/L, $K_f$is the capacity of the adsorbent in mg/g and n is the adsorption constant for freundlich in L/mg, usually greater than one. It can be stated that, if the 1/n value is below unity, this implies that the adsorption process is chemical; if the value is above unity, adsorption is a favourable physical process [77].

2.3 Adsorption kinetic models

Kinetic performance of a given adsorbent is of utmost important to get an indication about the solute uptake rate. It determines the residence time required to complete the adsorption reaction [78]. The solute uptake rate is very important when designing the adsorption system in pilot scale application. Due to the importance, the kinetic studies have been performed in majority of studies[63, 64]. According to the reviewed literature, pseudo-second order kinetic model was the frequently fitted model with aqueous chromium adsorption on to different magnetic nanosorbents.

Pseudo-second-order rate equation can be represented as follows.

$$\frac{dq_t}{d_t} = k_2(q_e - q_t)^2 \qquad (5)$$

It can be simplified and expressed in linearized form as below.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (6)$$

Where $k_2$is the pseudo-second order rate constant of adsorption in (g/mg min), $q_e$and q_t is the amount of sorbate adsorbed at equilibrium time and *t* time respectively, in mg/g and *t* is the contact time in minutes.

III. Conclusions

This review article covers the recent studies done for the aqueous hexavalent chromium removal using iron oxide magnetic nanosorbents. From the wide range of published work, it is evident that, adsorption capacity is mainly depending on the solution pH, temperature, initial contaminant concentration, adsorbent dosage and competitive influence of other coexisting ions in the water system. Majority of the experimental results claimed that, the optimum pH value for chromium adsorption onto iron oxide nanoparticles are within the range of 2-3. This is attributed to the fact that, Cr(VI) ions exist mainly in the form of $HCrO_4^-$ in the lower pH range, while CrO_2^{4-} is the dominant species at higher pH range. The adsorption mechanisms involved mainly are, electrostatic attraction followed by redox process, ion exchange and surface complexation. This review article also revealed that, in majority of cases, the adsorption isotherms are well fitted with Langmuir and/or Freundlich models and kinetics are in accordance to pseudo second order kinetics model.

The direct comparison of adsorption capacities are difficult due to the inconsistency of the test conditions. In some studies, removal percentage values are presented which is not illustrating the actual performance of the adsorbent. Therefore, it is reliable to consider the adsorption capacity value. The adsorption experiments with actual industrial wastewaters are recommended, as they are more complex solutions consist of different ions and, the performance of adsorbent may be considerably different from the performance in the laboratory prepared single ion solution.

Cost estimations are only rarely reported which is worthwhile to add. Regeneration of the magnetic nanomaterials is also an important aspect where, the cost can be significantly reduced during the industrial application. By considering all the facts, it can be concluded that magnetic nanomaterials are a potentially useful adsorbent for the aqueous hexavalent chromium removal, but still needs further work to develop the systems to apply them in industrial scale.

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