

A review on adsorptive remediation of Cr (VI) by magnetic iron oxides and their modified forms

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ABSTRACT

Cr (VI) is highly toxic, carcinogenic and bio accumulative to living organisms. Its extensive industrial applications contaminate the natural aqueous ecosystems. Different techniques such as photocatalysis, adsorption, reverse osmosis, ion exchange, chemical precipitation, electrochemical reduction, solvent extraction etc. have been investigated to remove hexavalent chromium from contaminated water. Among these, adsorption is deliberated as the most effective and promising process because it is easy to design, simple to operate and suitable to avoid formation of secondary pollutants. Various adsorbents such as clay minerals, biosorbents, industrial wastes and magnetic nanomaterials have been used for the remediation of Cr (VI). The use of magnetic nanomaterials as adsorbents for removal of heavy metals has attracted much attention in recent years because of their large surface area and superparamagnetic characteristics. These materials not only exhibited high adsorption capacity but also could easily be recycled by applying an external magnetic field, making the separation process much easier. In this review, the adsorption behavior of different iron oxides such as maghemites, magnetites, ferrites and their modified forms towards the removal of Cr (VI) was discussed. The present review focuses on adsorption mechanism of Cr (VI) through the evaluation of adsorption capacities. Kinetics, thermodynamics and equilibrium studies for the adsorption process were depicted briefly. Optimum adsorption conditions (initial Cr (VI) concentration, pH, contact time, adsorbent dose and temperature), thermodynamic properties (ΔH° , ΔG° , ΔS°), kinetic model, fitted isotherm, adsorption mechanism and maximum adsorption capacities were listed in the table.

Keywords: Iron oxides; Adsorption; Magnetic; Cr (VI); Adsorption Capacity.

1. INTRODUCTION

Wastewater containing venomous heavy metal ions like Cr (VI), Cd (II), Hg (II) and Pd (II) is released into the natural aqueous environment through electroplating, leather tanning, wood preservation, pulp processing and steel manufacturing. This reckless discharge into water ecosystem not only adversely affects the downstream users but also aquatic life [1, 2]. Among these heavy metal ions, Cr (VI) is deliberated as most priority contaminant due to its exceptionally high mobility and solubility in aqueous medium, tendency to accumulate in the organisms and carcinogenic effect. The toxic level of Cr (VI) is fixed 0.005 ppm in wastewater by World Health Organization (WHO) [3-5]. Therefore, numerous strategies such as reverse osmosis, ion-exchange, membrane filtration, ultra-filtration, electro dialysis, chemical precipitation, solvent extraction, photocatalysis and adsorption have been applied for the removal of Cr (VI) from the contaminated water before its discharge to water bodies [6-12]. However, adsorption is commonly used as a benevolent technique for remediation of Cr (VI) because it is easy to design, simple to operate and suitable to avoid formation of secondary pollutants [13-16]. Clay minerals, biosorbents, industrial wastes and nanomaterials have extensively been studied for the adsorptive removal of Cr (VI) [17-21]. Recently, nanomaterials gain great

attentions for their wide applications in the field of environmental purification, energy generation and storage due to their fascinating properties like high surface area, abundant reaction sites, tuneable pore structure etc. [22-27]. Different nanomaterials like layer double hydroxides, iron oxides, metalorganic frame works, etc. are used for adsorption of Cr (VI). Use of iron oxides for adsorption of heavy metals have attracted much attention because of their large surface area and superparamagnetic characteristics [28-30]. These materials not only exhibited high adsorption capacity [31] but also could easily be separated from the treated solution by the application of an external magnetic field [32] making separation process much easier. Present review reports on the adsorption behavior of iron oxide nanoparticles such as maghemites, magnetites, ferrites and their modified forms towards removal of Cr (VI). An overview of adsorption mechanism through the evaluation of adsorption capacities was presented. Kinetics, thermodynamics and equilibrium studies for the adsorption process were depicted briefly. Optimum adsorption conditions (initial Cr (VI) concentration, pH, contact time, adsorbent dose and temperature), thermodynamic properties (ΔH° , ΔG° , ΔS°), kinetic model, fitted isotherm, adsorption mechanism and maximum adsorption capacities were listed in the Table 1.

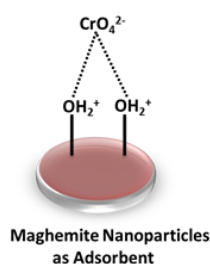
2. ADSORPTION OF Cr (VI) ON TO IRON OXIDES

2.1 Adsorption behavior of maghemite nanoparticles towards removal of Cr (VI).

Maghemite nanoparticles ($\gamma\text{-Fe}_2\text{O}_3$) appear to be promising adsorbents for Cr (VI) removal as these are inexpensive, readily

available and can easily be separated. Nanoparticles of maghemite prepared by sol-gel method possessed saturation moment of 3.3 emu g⁻¹ which indicated that these particles responded well to the magnetic fields without any permanent magnetization and hence

could easily be separated from the treated solution by using an external magnetic field. Moreover, these particles have shown a rapid rate of adsorption of Cr (VI) due to the presence of active sites at the exterior part of the adsorbent that facilitates quick interaction of Cr (VI) species. Maximum adsorption capacity observed by these particles was found to be 19.2 mg g^{-1} [33]. Adsorption process involves electrostatic attraction between anionic Cr (VI) species and protonated surface hydroxyl groups of the adsorbent at low pH (2.5) as shown in the scheme 1. A similar mechanism for adsorption of Cr (VI) was also reported for mesoporous magnetic iron-oxide ($\gamma\text{-Fe}_2\text{O}_3$). The adsorbent exhibited maximum adsorption capacity of 15.6 mg g^{-1} with a faster rate of adsorption and the adsorbent was completely separated from the solution by using an external magnetic field [34].



Scheme 1. The Plausible mechanism of adsorption of Cr (VI) onto Maghemite nanoparticles.

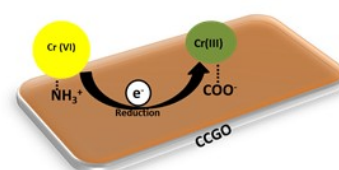
Adsorption capacity of maghemite nanoparticles is influenced by surface functionalisation. Singh et al. reported that functionalisation of starch on maghemite nanoparticles provides additional hydroxyl groups which increase the number of surface active sites and enhances adsorption of Cr(VI) species with an improved adsorption capacity of 27.06 mg g^{-1} [35]. A reverse trend in adsorption of Cr (VI) was observed for humic acid modified maghemite nanoparticles as a coating of maghemite nanoparticles with humic acid decreased the adsorption sites as well as increased the number of negatively charged carboxylic groups at the surface resulting in electrostatic repulsion of oxyanionic Cr (VI) species [36].

2.2 Adsorptive removal of Cr (VI) over magnetite nanoparticles.

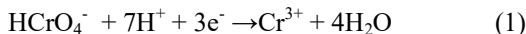
Nanoparticles of magnetite are extensively used for adsorption of Cr (VI) due to their easy methods of preparation, good chemical stability, low toxicity, high surface area and a large number of surface active sites. Large saturation magnetization with superparamagnetic properties enabled them to be separated by employing an external magnetic field and could easily be recovered from treated solutions. Asuha et al reported that surfaces of mesoporous magnetite (Fe_3O_4) get protonated at low pH resulting in positively charged surface groups ($-\text{FeOH}_2^+$). These groups adsorb oxyanionic species of Cr (VI) by coulombic force to get adsorption capacity of 15.4 mg g^{-1} [37]. The maximum adsorption capacity of 13.3 mg g^{-1} and 18.36 mg g^{-1} were obtained from magnetite nanoparticles prepared by electrochemical [38] and coprecipitation methods [39] respectively. Porous magnetite nanospheres exhibited adsorption capacity of 8.90 mg g^{-1} at 45°C [40].

Magnetite nanoparticles show strong tendency to form aggregate due to their high specific surface area as well as strong dipole-dipole attractions. As a result, their stability is decreased

and their applications are limited. In order to prevent aggregation and enhance adsorption capacity, surfaces of magnetite nanoparticles are modified [41]. Tetramethylammonium hydroxide modified magnetite nanoparticles exhibited an improved adsorption capacity of 34.9 mg g^{-1} at 45°C [42]. Burks et al. reported that 3-Mercaptopropionic acid coated Fe_3O_4 nanoparticles exhibited an adsorption capacity of 45 mg g^{-1} at pH 1.0. This increase in adsorption capacity may be attributed to the bonding of negatively charged Cr (VI) species with the $-\text{SO}_3\text{H}$ groups formed by oxidation of 3-Mercaptopropionic acid [43]. Maximum adsorption capacity of 60.25 and 61.35 mg g^{-1} were shown by ethylenediamine functionalized Fe_3O_4 nanochains [44] and ethylenediamine functionalized Fe_3O_4 magnetic polymer [45] respectively. It is further increased to 99 mg g^{-1} by MCM-41 modified magnetite nanoparticles [46]. Li and his coworkers used magnetically separable cyclodextrin-chitosan modified graphene oxide (CCGO) for removal of Cr (VI) from aqueous solution. The surface hydroxyl groups and magnetic cyclodextrin-chitosan present in the adsorbent are homogeneously distributed on the surface of graphene oxide and the adsorption process involves the following steps. (i) Negatively charged Cr (VI) species get attracted by protonated amine groups of the adsorbent in acidic medium due to electrostatic attraction [47]. (ii) In acidic medium, Cr (VI) is partial reduced to Cr (III) with the help of π – electrons present on the carbocyclic six membered ring of cyclodextrin-chitosan modified graphene oxide. (iii) Cr (III) species so formed are either released into the solution due to electrostatic repulsion of protonated amine groups or Cr (III) get bound with negatively charged groups (COO^-) present on the surface of adsorbent by electrostatic attraction. (iv) Cr (VI) and Cr (III) species are inserted into the cavities of cyclodextrin to form stable host-guest inclusion complexes. The possible mechanism of adsorption was shown in scheme 2. Maximum adsorption capacity achieved by this adsorbent was found to be 67.66 mg g^{-1} [48]. Magnetic chitosan graphene oxide nanocomposite (CGO) exhibited maximum adsorption capacity of 101.6 mg g^{-1} [49]. Less adsorption capacity observed by the former compared to chitosan graphene oxide nanocomposite may be attributed to the chemical cross linking of chitosan with glutaraldehyde which decreases the number of available $-\text{NH}_2$ and $-\text{OH}$ groups which are responsible for adsorption [50]. Improved adsorption capacity of 117.94 mg g^{-1} was obtained by magnetic mesoporous titanium dioxide modified graphene oxide (MTGO) because magnetic mesoporous titanium dioxide spheres prevent graphene oxide from agglomeration and edges of graphene oxide sheets could spread out of the spheres to a large extent with enough adsorption sites. The presence of Cr (VI) and Cr (III) species on the surface of adsorbent confirmed that removal occurs through partial Cr (VI) reduction in acidic medium as shown in the Eqn. 1.

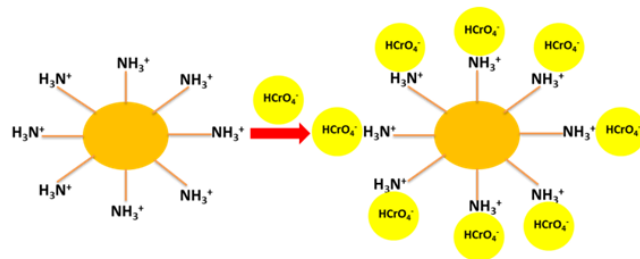


Scheme 2. Mechanism of adsorption of Cr (VI) onto cyclodextrin-chitosan modified graphene oxide.



The mechanism of adsorption involves electrostatic attraction of negatively charged Cr (VI) species by protonated hydroxy groups present on the surface of adsorbent followed by partial reduction of Cr (VI) species into Cr (III) with the help of pi- electrons of the carbocyclic six membered ring of the adsorbent. Cr (III) species so obtained either enter into the solution due to electrostatic repulsion from protonated hydroxy groups or get bound with the surface of adsorbent by the electrostatic attraction of COO-groups [51,]. In addition to this, the metal ions are bound with the oxygen atoms of plentifully available oxygen containing functional groups of the adsorbent surface. Moreover, the protonated -NH₂ groups of ammoniated mesoporous TiO₂ adsorb Cr (VI) species through electrostatic attraction [52].

Fe₃O₄ was modified with polymer nanocomposites such as polyaniline, polypyrrole, tetraethylenepentamine and m-phenylenediamine [53-59]. As nanosized polypyrrole is considered as a good adsorbent [60] for remediation of Cr (VI), Fe₃O₄ functionalised polypyrrole nanocomposite was prepared and subjected for adsorption of Cr (VI). The adsorbent exhibited 169.5 mg g⁻¹ [61]. Enhanced adsorption capacity of 238 mg g⁻¹ was observed by Fe₃O₄/glycine doped polypyrrole (FGP) nanocomposite at pH 2.0. The amine groups of glycine are protonated at low pH and hence, the negatively charged HCrO₄⁻ gets adsorbed on the surface of adsorbent by the protonated amine groups through ionic interaction resulting an enhanced adsorption capacity. Adsorption mechanism was given in scheme 3 [62].



Scheme 3. Mechanism of adsorption of Cr(VI) onto FGP nanocomposite.

2.3 Adsorption of Cr (VI) by Ferrites.

Ferrites are also used for remediation Cr (VI) as they can easily be separated by employing an external magnetic field [63-66]. Mesoporous NiFe₂O₄ samples with high surface area adsorbed Cr (VI) species from aqueous solution at lower pH through coulombic attraction with a loading capacity of 43.68 mg g⁻¹. Authors have reported that these samples possessed high magnetic sensitivity due to which they could easily be recovered from the treated solution by employing an external magnetic field and hence could efficiently be reused. [67]. CaFe₂O₄ nanoparticles were employed for the removal of Cr (VI) as these are considered to be relatively more biocompatible due to inherent nontoxic nature of calcium. Maximum adsorption capacity obtained by these nanoparticles is 124.11 mg g⁻¹ at pH 2.0 [68]. Magnetic properties of ferrites are modified by doping with rare earth ions [69]. Kuai and his co-workers synthesized nano sized particles of Ce³⁺ doped magnetic zinc ferrites with formula ZnCe_xFe_{2-x}O₄ [32]. Maximum adsorption capacity for the sample with formula ZnCe_{0.03}Fe_{1.97}O₄ was found to be 57.24 mg g⁻¹.

Table 1. Optimum adsorption conditions like initial Cr(VI) concentration, pH, contact time, temperature, adsorbent dose, maximum adsorption capacity, mechanism of adsorption, thermodynamic parameters, kinetic model and fitted isotherm for magnetic iron oxides and their modified forms.

Name of the adsorbent	Max.Ads Capacity (mg g ⁻¹)	Optimum pH	Temperature (°C)	Initial Cr(VI) concentration (mg L ⁻¹)	Adsorbent dose (g L ⁻¹)	Contact Time (Minutes)	Fitted Isotherm	Kinetic model	Thermodynamic parameters	Mechanism of adsorption	Reference
Mesop. γ-Fe ₂ O ₃	15.6	2.5	22	5-100	1.25	20	-----	-----	-----	Electrostatic attraction	34
Maghemite nanoparticles	19.2	2.5	25	5-200	5.0	15	Freundlich	-----	-----	Electrostatic interaction and ion exchange	33
Starch functionalised Maghemite nanoparticles	27.06	2.0	30	12	4.0	1440	Freundlich	Pseudo second order	ΔH = +ve, endothermic ΔG = -ve, spontaneous ΔS = +ve,	Electrostatic attraction	35
magnetite (Fe ₃ O ₄) nanopowder	15.4	6.0	-----	5-100	1.5	30	Langmuir	-----	-----	Electrostatic attraction	37
Magnetite Nanoparticles	18.36	5.5	100-400	2.0	60	Freundlich	Pseudo second order	Electrostatic attraction	39
Magnetite Nanoparticles	13.3	3.5	20	80	2.0	30	Langmuir	Pseudo second order	Electrostatic attraction	38
Magnetite nanospheres	8.90	4.0	45	10-100	2.0	2880	Redlich-Peterson	Pseudo second order	Complexation, Electrostatic attraction	40
Magnetite Nanoparticles	34.9	2.0	45	2-100	2.0	1440	Sips	Pseudo second order	Electrostatic attraction	42
3Mercaptopropionic acid coated Fe ₃ O ₄ nanoparticles	45	1.0	25	50	0.5	60	Freundlich	Pseudo second order	surface complexation	43
Ethylenediamine functionalized Fe ₃ O ₄ nanochains	60.25	2.0	25	40	1.0	360	Langmuir	Electrostatic attraction, reduction of Cr(VI) to Cr (III), coordination interaction of Cr (III).	44
Ethylenediamine	61.35	2.5	35	10-150	1.25	60	Langmuir	Pseudo	45

Name of the adsorbent	Max.Ads Capacity (mg g ⁻¹)	Optimum pH	Temperature (°C)	Initial Cr(VI) concentration (mgL ⁻¹)	Adsorbent dose (g L ⁻¹)	Contact Time (Minutes)	Fitted Isotherm	Kinetic model	Thermodynamic parameters	Mechanism of adsorption	Reference
amine functionalized Fe ₃ O ₄ magnetic polymer								second order			
CCGO	67.66	3.0	30	50	1.0	-	48
CGO	101.6	3.0	25	10-500	1.0	300	Langmuir, Redlich–Peterson	Pseudo second order	ΔH° = +ve ΔG° = -ve ΔS° = +ve	Ion exchange	49
MCM-41/Fe ₃ O ₄	105	2.0	25	106-156	1.0	Freundlich	46
Fe ₃ O ₄ / polypyrrole nanocomposite	243.9	2.0	45	200-600	2.0	30-180	Langmuir	Pseudo second order	ΔH = +ve, endothermic ΔG = -ve, spontaneous ΔS = +ve,	Anion exchange	61
Fe ₃ O ₄ glycine - polypyrrole nanocomposite	303	2.0	45	200-650	2.0	30-180	Langmuir	Pseudo second order	ΔH = +ve, endothermic ΔG = -ve, spontaneous ΔS = +ve,	Electrostatic attraction followed by reduction of Cr(VI) to Cr (III)	62
NiFe ₂ O ₄	43.68	2.0	25	10-250	2.0	120	Langmuir	Pseudo second order	Electrostatic attraction	67
CaFe ₂ O ₄	124.11	2.0	30	50	1.0	40	Langmuir	Pseudo second order	ΔH = -ve, exothermic ΔG = -ve, spontaneous ΔS = -ve,	Electrostatic attraction	68
ZnCe _{0.03} Fe _{1.97} O ₄	57.24	2.0	25	60	0.5	4320	Langmuir	Pseudo second order	Electrostatic attraction	32

4. CONCLUSIONS

Adsorption behavior of iron oxides and their modified forms towards removal of Cr (VI) were reviewed. The mechanism of adsorption was briefly discussed. Adsorption process mostly occurs at low pH through electrostatic attraction between anionic Cr (VI) species and protonated surface hydroxyl groups of iron oxides. The modified forms exhibit high adsorption capacity basically due to strong interaction between protonated amine groups and negatively charged Cr (VI) species through electrostatic attraction. Being magnetic in nature these adsorbents can easily be separated from the treated solution by application of

an external magnetic field. This finds a major advantage of these adsorbents in the field of waste water treatment towards remediation of Cr (VI). However, the practical application of such adsorbents really faces a number of challenges such as relatively low adsorption capacity and technical difficulties for their industrial use. Therefore, tremendous efforts are necessary from the scientists and engineers to enable these challenging adsorbents for efficient application in the removal of Cr (VI) from laboratory scale to industrial scale.

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