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Author(s): Jain, Monika; Yadav, Mithilesh; Kohout, Tomas; Lahtinen, Manu; Garg, Vinod Kumar; Sillanpää, Mika

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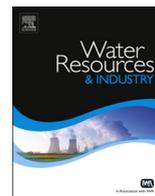
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Development of iron oxide/activated carbon nanoparticle composite for the removal of Cr(VI), Cu(II) and Cd(II) ions from aqueous solution



Monika Jain^{a,*}, Mithilesh Yadav^b, Tomas Kohout^c, Manu Lahtinen^d,
Vinod Kumar Garg^e, Mika Sillanpää^a

^a Laboratory of Green Chemistry, Department of Chemistry, Lappeenranta University of Technology, Sammonkatu 12, FI-50130 Mikkeli, Finland

^b Department of Chemical and Materials Engineering, Chang Gung University, 259, Wen-Hwa, 1st. Road, KweiShan, 33302 Taoyuan, Taiwan

^c Department of Physics, University of Helsinki, P.O. Box 64, FI-40014, Finland

^d Department of Chemistry, University of Jyväskylä, P.O. Box 35, FI-40014 JY, Finland

^e Centre for Environmental Sciences and Technology, Central University of Punjab, Bathinda 151001, India

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ABSTRACT

Iron oxide (Fe₃O₄) and iron oxide/activated carbon (Fe₃O₄/AC) were fabricated by co-precipitation method for the removal of Cr(VI), Cu(II) and Cd(II) ions from aqueous solution in batch mode. These nanoparticles were characterized by BET, FTIR, XRD, SEM/TEM and VSM. The optimum conditions for the removal of ions were pH = 2 for Cr(VI) and 6 for Cu(II) and Cd(II), initial metal ion concentration = 50 mg L⁻¹, nanoparticle dose = 50 mg/10 mL, temperature = 25 ± 1 °C, shaking speed = 180 rpm and contact time = 3 h. The equilibrium data of ions sorption were well described by Langmuir, Freundlich, Redlich-Peterson and Intraparticle Diffusion model. The R² values obtained by Langmuir model were highest by Fe₃O₄/AC for Cr(VI) = 0.9994, Cu(II) = 0.9998 and Cd(II) = 0.9750. The temperature dependent study in the range of 288–328 K confirmed that the adsorption process was endothermic in nature. Desorption studies with 0.1 M HCl stated that these nanoparticles can be regenerated effectively and can be used after four adsorption-desorption cycles without any mass loss.

1. Introduction

Today, water contamination with different pollutants (mainly heavy metals and dyes) has become a major environmental problem and a threat to the well being of living organisms [1–3]. Heavy metals are non-biodegradable, persistent, carcinogenic and toxic in nature and are widely distributed in the environment. They bioaccumulate in living organisms through food chain and their accumulation causes different diseases and malfunctions. Cadmium, chromium and copper are among few heavy metals that are discharged from several industrial effluents.

Cadmium is liberated into the environment from steel production, cement manufacture, Ni-Cd battery manufacture, cadmium electroplating, phosphate fertilizers etc. [4]. According to the World Health Organization (WHO) [5] guidelines, the maximum concentration for cadmium in drinking water was set at 0.003 mg L⁻¹ in 2010. Zaini et al. [6] reported that bivalent cadmium causes several deformities in humans such as muscular cramps, pulmonary problems, renal degradation, proteinuria, skeletal deformity,

* Corresponding author.

E-mail address: monika.biorem@gmail.com (M. Jain).

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testicular atrophy etc.

Hexavalent chromium is another heavy metal in the environment released from various sources like electroplating, leather tanning, mining, textile and fertilizer industries. It is toxic, carcinogenic and mutagenic to human beings and animals [7,8]. It causes cancer in digestive tract and lungs, epigastric pain, nausea, diarrhea, vomiting and hemorrhage as stated by Mohanty group [9]. The maximum permissible limit for hexavalent chromium in drinking water is 0.05 mg L^{-1} [10].

Copper is another essential element that is required for the synthesis of enzymes, tissues and bone development. The sources of copper from various industries include smelting, mining, electroplating, surface finishing, electric appliances, electrolysis and electrical components [11]. It is toxic and carcinogenic when ingested in large amounts and causes headache, vomiting, nausea, liver and kidney failure, respiratory problems and abdominal pain [12,13]. The maximum permissible limit set by USEPA for the release of copper in industrial effluents is 1.3 mg L^{-1} . Thus, the effluents containing such kind of heavy metals which are harmful to the living organisms must be treated before discharging into ambient environment. In this regard, nanotechnology has been the focus of researchers since a couple of years.

Iron oxide nanotechnology has been gaining the attraction of research society in solving the environment related problems [14,15]. This is because iron oxide is very useful in removing various kinds of air, water and soil contaminants through adsorption and photo-degradation. In addition to this, the deteriorating quality of water has led the researchers to use iron oxide nanoparticles as new generation adsorbents for water treatment [16]. Iron oxide is great adsorbent as it has high surface area-to-volume ratio, its surface can be modified, excellent magnetic properties, great biocompatibility, ease of separation using external magnetic field, reusability and comparatively low cost [17,18]. Also, it can coordinate with other elements due to variable oxidation states. Despite the above, iron oxide has one disadvantage that its particles aggregate due to their large surface-to-volume ratio and low surface energy [19,20]. To control this, surface modification is required to ensure the stability of particles.

Surface modification of iron oxide nanoparticles can be performed through coating, stabilization and functionalization. In surface coating, iron oxide attracts water molecules (hydrophilicity) and doesn't form clusters due to the dispersion of particles [21]. The surface modification of iron oxide by activated carbon using coating technique improves their sorption capability because surface coating phenomenon helps in converting the closely - packed cubic geometry of magnetic nanoparticles into compact and strong [20]. Few examples can be found in the literature wherein the surface coated iron oxide nanoparticles have been utilized for the removal of heavy metals and dyes. Tailored EDTA di-anhydride treated magnetic Fe_3O_4 baker's yeast biomass (EFB) was investigated by Xu et al. [22] for the removal of Pb(II) and Cd(II) ions from aqueous solution. Wannahari et al. [23] reported that sugarcane bagasse derived nanomagnetic adsorbent composite can remove Cu(II) from aqueous solution. Shen et al. [24] found that the adsorption capacity of iron oxide nanoparticles for the removal of Ni(II), Cu(II), Cd(II), Cr(VI) from contaminated water was high. Ghasemi group [19] reported high sorption capacity of surface coated iron oxide nanoparticles. Kakavandi group [25] studied the adsorption of Pb(II) onto Fe_3O_4 /activated composite. Removal of dye from aqueous solution using Fe_3O_4 -activated carbon nanocomposite was studied by Gholamvaisy et al. [26]. Affam et al. [27] found that the iron oxide/activated carbon composite can remove boron and organics from wastewater. In the similar way, it has also been found that [28–34] activated carbon/iron oxide composite is useful in removing different kinds of contaminants like trinitrophenol, phosphate, atrazine, lead, arsenic, mercury and methylene blue dye from aqueous solutions.

It is well-documented that, agricultural waste has huge scientific, social and economic significance as it is abundantly available at no or little cost, require simple processing, easy to handle and no regeneration is required. In 2013, our group [35] treated deseeded sunflower heads with formaldehyde (to inhibit leaching of soluble organic matter from lignocellulosic materials). These treated sunflower heads (FSH) were then used for sequestering chromium ions from synthetic and steel industry wastewater. The adsorption capacity of FSH was found to be 7.9 mg g^{-1} for Cr(VI) at pH 2.0 and a temperature of 25°C from synthetic wastewater. While, the percent removal of Cr(VI), Cu(II) and Cd(II) from steel industry wastewater was 45%, 40.8% and 35.1% respectively at their optimum pH i.e. 2.0, 5.0 and 6.0.

A review of literature on using sunflower and its parts (seed husk, seed hull, dried leaves, stalks) for the removal of heavy metals and dyes from wastewater revealed that very limited information is available. Some of the studies carried out by various researchers are given here in brief. Sun and Xu [36] investigated sunflower stalks for the removal of methylene Blue, Basic Red 9, Congo Red and Direct Blue 71 from aqueous solutions. Benaissa and Elouchdi [37] evaluated the potential of dried sunflower leaves for removing copper ions from single metal ion solution in a well-stirred batch reactor. Thinakaran et al. [38] explored the adsorption of Acid Violet 17 using activated carbons prepared from sunflower seed hull (SSH) treated with sulphuric acid at three different temperatures. The adsorption efficiency of crushed and uncrushed sunflower husks for removal of methylene blue from aqueous solution was investigated by Soldatkina et al. [39]. Sunflower stalks modified by nitric acid activation were used by Hussein [40] for the removal of copper from wastewater in batch and fixed bed mode. Activated carbon (via microwave induced K_2CO_3 activation) was prepared by Foo and Hameed [41] from sunflower seed oil residue which is a by-product of sunflower seed oil refining industry. They utilized it for the removal of methylene blue and acid blue 15 from aqueous solution. The sunflower hulls are a waste material that originates from food industry. These hulls were used by Witek-Krowiak [42] for the biosorption of Cu(II) ions from aqueous solution. Zou et al. [43] demonstrated that the activated carbon prepared from sunflower seed hull (an abundant agriculture byproduct) was highly porous, inexpensive and efficient adsorbent for the removal of Cr(VI). Feizi and Jalali [44] explored sunflower stalks and leaves for the removal of Cd, Cu, Ni, Zn, Mn, Fe in single and competitive batch mode from aqueous solution. Saleh and Gupta [3] prepared biochar from sunflower seed husk and found its adsorption potential in removing copper ions from wastewater. Srisorachatr [45] prepared activated carbons from sunflower seed husks (SSH) by chemical activation with potassium carbonate and zinc chloride solution followed by carbonization and used them for removal of Pb(II), Ni(II), Zn(II) and Cd(II) from aqueous solution.

As it is clear from the review of literature that less research work has been carried out on unmodified sunflower head and stem

waste. Besides this, only few studies have been reported on surface modification of iron oxide by using sunflower activated carbon for developing magnetic activated carbon nanocomposite. This combination has transformed the sunflower waste into useful magnetic activated carbon sorbents for removing toxic ions from wastewater. Another advantage is that the loaded adsorbents could be easily separated from the aqueous solution using magnet instead of centrifugation thus conserving energy.

Based on the aforementioned properties, agricultural waste (sunflower head waste) was chosen as a raw material which was combined with iron oxide nanoparticles as it was anticipated that this twofold combination of adsorption and magnetic separation would make the wastewater treatment process ecofriendly, effective and economically more attractive. In this study, material preparation, characterization and batch-type removal experiments were carried out wherein the feasibility of the above described composite for the removal of heavy metals [Cr(VI), Cu(II) and Cd(II)] from aqueous solution were investigated by varying the process conditions.

2. Material and methodology

2.1. Chemicals

All the chemicals used in this study were of analytical grade (Sigma Aldrich, FINLAND). Stock solutions of 1000 mg L^{-1} concentration of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were prepared in ultra-pure water acidified with nitric acid to prevent hydrolysis. The working solutions were made by diluting the stock solution. The pH of the solution was adjusted by adding 0.01 M HCl or 0.01 M NaOH and measured using electronic pH meter (WTW inoLab pH 730, Germany). The concentration of heavy metals in the aqueous solution was measured using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) [model iCAP 6000 (Thermo Electron Corporation, UK)] at a wavelength of 283.563 nm for Cr(VI), 324.75 nm for Cu(II) and 228.802 nm for Cd(II).

2.2. Preparation of nanoparticles

2.2.1. Preparation of activated carbon by sunflower head waste (chemical activation method)

Chemical activation can be carried by any of the mineral acids like HCl, HNO_3 , H_2SO_4 , phosphoric acid as it increases the porosity of the carbon structure during the acid treatment. Impregnation ratio also strongly affects the characteristics of activated carbon (AC). As our's was an agricultural waste, so it contained large amount of lignin and if the percentage of lignin is more, then sulphuric acid activation leads to an increase in BET surface area [46].

Table 1 depicts that, the surface area, pore volume and pore width, all increased after activation with sulphuric acid, as this process leads to an extensive increase in the porosity of the material (Fig. 5). If we compare the surface area of the ACs prepared by sulphuric acid, phosphoric acid, zinc chloride, then, it was found that the surface area of sulphuric acid treated AC was highest [47]. High surface area and pore structure are the basic parameters for an effective adsorbent and these parameters are introduced by chemical activating agents like sulphuric acid.

Activated Carbon prepared from sunflower head waste was synthesized as per the method reported by [48]. Sunflower head waste biomass was crushed into fine powder in a steel mill. Crushed powder was boiled in distilled water and cooled. The procedure of boiling and cooling was repeated till the supernatant was colorless. The washed crushed powder was rinsed with 1% HCl, washed again with distilled water till the wash water became colorless. The powder was dried at 80°C for 24 h in a hot air oven to get rid of moisture and volatiles. Pretreated sunflower head waste powder was treated with concentrated sulphuric acid in the ratio of 1:2 (w/v). It was then washed with distilled water continuously to remove free acid and soaked in 1% sodium bicarbonate solution overnight to neutralize the acid. It was then washed with distilled water and dried at 80°C in hot air oven for 24 h. The dried material was subjected to thermal activation in a muffle furnace at 500°C flushed with nitrogen gas at a flow rate of 20 mL min^{-1} for 1.0 h. The material was cooled in N_2 atmosphere, washed with ultra-pure water and dried at same conditions as mentioned above. The activated carbon (namely AC) was sieved from the standard mesh of size $250 \mu\text{m}$ and stored in a vacuum desiccator for further use.

2.2.2. Preparation of iron oxide/activated carbon nanocomposite ($\text{Fe}_3\text{O}_4/\text{AC}$) and iron oxide nanoparticles (Fe_3O_4)

The iron oxide/activated carbon nanocomposite ($\text{Fe}_3\text{O}_4/\text{AC}$) was prepared as reported by [14] with some modification. A required amount of AC was dispersed in 400 mL solution of 7.8 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (28 mM) and 3.8 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (14 mM) with vigorous stirring on a magnetic stirrer at 700 rpm at $70\text{--}80^\circ\text{C}$. The NaOH (5.0 M) solution was added drop wise into the above suspension under vigorous stirring at 80°C until pH raised to 10–11 to precipitate the hydrated iron oxide. The suspension was stirred further on a magnetic stirrer at 80°C for 1.0 h. Next, it was aged at room temperature for 24 h. The $\text{Fe}_3\text{O}_4/\text{AC}$ nanocomposite were separated by a magnet and washed repeatedly with distilled water and ethanol till neutral pH. They were then dried in hot air oven at

Table 1

Surface area, pore volume and average pore diameter of Sunflower Head Waste, Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{AC}$.

Material	Surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Average pore diameter (\AA)
Sunflower Head Waste	0.99	0.0007	3.037
Fe_3O_4	47.87	0.0355	3.245
$\text{Fe}_3\text{O}_4/\text{AC}$	51.1	0.0386	3.293

80 °C for 12 h. After drying, the nanoparticles were crushed in mortar and pestle and stored in air tight plastic containers for further use. In addition, the procedure for synthesis of iron oxide nanoparticles (Fe_3O_4) was similar as mentioned above except that no AC was added.

2.3. Characterization of nanoparticles

2.3.1. Surface area analysis

The BET surface area and pore volume of the nanoparticles were measured by BJH desorption method in N_2 atmosphere at 77 K in a Quantachrome surface area analyzer (model Autosorb 1). The nanoparticles before measurement were degassed at 200 °C for 24 h in order to remove the moisture.

2.3.2. pH – point zero charge (pH_{pzc})

The pH_{pzc} was measured using 0.01 M NaCl aqueous solution. The initial pH of the solution was set in the range of 2–12 with 0.1 M HCl/NaOH and 50 mL of this solution was added to the conical flasks containing 0.15 g of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{AC}$. The flasks were agitated in an orbital shaker for 48 h and the final pH of the solution was determined using pH meter. The value of pH_{pzc} was obtained by plotting the graph between pH_{final} versus $\text{pH}_{\text{initial}}$. The point of intersection of pH_{final} versus $\text{pH}_{\text{initial}}$ was the pH_{pzc} of the nanoparticles.

2.3.3. Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectra of native as well as Cr(VI), Cu(II) and Cd(II) loaded magnetic nanoparticles was recorded using FT-IR Spectrometer (BRUKER OPTIK GmbH, FT-IR Spectrometer VERTEX 70, Germany) between 4500 and 400 cm^{-1} at a resolution of 4.0 cm^{-1} taking 32 scans for each spectrum.

2.3.4. Powder X-ray diffraction studies (PXRD)

The diffraction data for the examined Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{AC}$ samples were acquired using powder X-Ray diffractometer (PAN analytical X'Pert PRO alpha 1) with monochromatic $\text{Cu-K}_{\alpha 1}$ radiation (primary beam Johansson monochromator; $\lambda = 1.5406\text{ \AA}$) at 45 kV and current of 30 mA. Data were recorded with position sensitive X'Celerator detector in a continuous scanning mode: 2θ -range of $10\text{--}70^\circ$ with a step size of 0.017° . Diffraction patterns were processed with PANalytical High Score Plus program (v. 4.5). Scherrer Eq. (1) was used for calculating the average crystal size of magnetic nanoparticles:

$$D = \left(\frac{k\lambda}{\beta \cos \theta} \right) \quad (1)$$

where D = average size of the crystals; K = shape-dependent Scherrer's constant (0.90); λ = radiation wavelength (1.5406 \AA); β_s = full width at half maximum intensity (FWHM given in radians); θ = Bragg's diffraction angle.

2.3.5. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS)

The texture and surface morphology of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{AC}$ were determined using a field emission Scanning Electron Microscope (model HITACHI S-4800) at an accelerating voltage of 30 kV with a working distance of 8.0 mm and an emission current of $20.0\text{ }\mu\text{A}$ of Tungsten filament. The SEM images were obtained at a magnification of 400 k. The elemental composition of the samples was obtained using Energy Dispersive X-ray Spectrometer (model EDAX TSL AMETEK, USA) in conjunction with SEM.

2.3.6. Transmission Electron Microscopy (TEM)

The particle size of the nanoparticles was determined using high-resolution aberration-corrected Transmission Electron Microscope (model JEOL-2200FS, Japan) operated at 200 kV. For sample preparation, the nanoparticles were dispersed in acetone for 30 min in a sonicator. The samples were then dropped on standard holey carbon films and dried at room temperature. They were then transferred to Cu grids (Agar Scientific, UK) for analysis in the microscope.

2.3.7. Magnetic properties (Vibrating Sample Magnetometer)

The magnetic hysteresis and susceptibility measurement of magnetic nanoparticles were measured using Vibrating Sample Magnetometer (Princeton Measurements Micromag Model 3900 VSM, USA) at room temperature at a maximum applied magnetic field of 1.2 T.

2.3.8. Thermogravimetric analysis (TGA)

The changes in the mass of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{AC}$ as a function of temperature in a defined and controlled environment from 26 to $1000\text{ }^\circ\text{C}$ were measured by TGA/DTG curves in N_2 atmosphere at a heating rate of $20\text{ }^\circ\text{C min}^{-1}$ (model NETZSCH TG 209F1 220-10-155-K, Germany).

3. Batch adsorption studies

The batch mode adsorption experiments were conducted to evaluate the removal of Cr(VI), Cu(II) and Cd(II) ions from aqueous

solutions. For the adsorption experiments, 10 mL solution of each ion of desired concentration (10–500 mg L⁻¹) at a predetermined initial pH [2.0 Cr(VI), 6.0 Cu(II) and Cd(II)] and nanoparticle dosage in 15 mL disposable, capped tubes at 26 ± 1 °C at an agitation speed of 180 rpm in a rotary shaker (model temperature controlled IKA KS 4000 ic, Germany) were agitated for 24 h. The nanoparticles were separated by strong magnet and the supernatant was collected by 0.20 µm polypropylene membrane syringe filter. Residual concentration of the metal ions in the solution was determined using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The percent metal removal (R %) was calculated using Eq. (2):

$$R(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

where C_i and C_e were the initial and equilibrium concentration of metals in the solution. The adsorption capacity (q_e) of the nanoparticles at equilibrium time was calculated using Eq. (3):

$$q_e(\text{mg/g}) = \left[\frac{C_i - C_e}{M} \right] \times V \quad (3)$$

where C_i and C_e are same as above. V is the volume of solution (L) and M is the mass of nanoparticles (in g) used.

4. Results and discussion

4.1. Characterization of nanoparticles

The data indicated that, the Sunflower Head Waste (SHW) has a very small surface area (0.99 m² g⁻¹) with a pore volume of 0.0007 cm³ g⁻¹ (Table 1). While, when SHW was converted into activated carbon (AC), the surface area increased to 25.07 m² g⁻¹. The surface area of Fe₃O₄ was found to be 47.87 m² g⁻¹ that further increased to 51.1 m² g⁻¹ when Fe₃O₄ was coated with AC. The pH_{pzc} (pH at point of zero charge) of Fe₃O₄ and Fe₃O₄/AC was found to be 5.2 and 7.04 respectively.

Adsorbents with diverse type of chemical groups like carboxyl, hydroxyl, ester, aldehyde, ketone etc. have the ability to bind with metal ions. Their affinity for metal uptake depends on factors like the number of sites, their accessibility, chemical form, affinity between binding sites and metal ions etc. [49]. The functional groups and their corresponding frequencies are shown in the FT-IR spectra of Fe₃O₄ and Fe₃O₄/AC and metal loaded Fe₃O₄ and Fe₃O₄/AC (Fig. 1). FTIR analysis indicated the presence of several strong absorption peaks. The presence of infrared absorption peaks at about 530.35, 528.42, 522.64, 568.21 cm⁻¹ in Fe₃O₄, Cr, Cu and Cd loaded Fe₃O₄ and 536.14, 534.29, 538.07, 530.67 cm⁻¹ in Fe₃O₄/AC, Cr, Cu and Cd loaded Fe₃O₄/AC respectively confirmed the presence of iron oxide nanoparticles with respect to characteristic stretching band of Fe–O onto their surface [24]. No other peak was found in Fe₃O₄ thus, indicating that it comprised of iron oxide only.

On the other hand, in Fe₃O₄/AC, the peak at 2341.29 cm⁻¹ is attributed to aromatic –C=C. The strong –C–O band at 1037.57 cm⁻¹ due to –OCH₃ group indicated the presence of lignin group in the sunflower head which is the characteristic peak of polysaccharides. The band at 1585.28 cm⁻¹ in chromium loaded Fe₃O₄/AC may be due to asymmetric stretching of –C–O bond, stretching of aromatic –C=C bond or due to amide stretching. In copper loaded Fe₃O₄/AC, the absorption peak at 3423.22 cm⁻¹ may be attributed to –NH/–OH stretching indicating the existence of free and intermolecular bonded hydroxyl group due to alcoholic or phenolic functions and

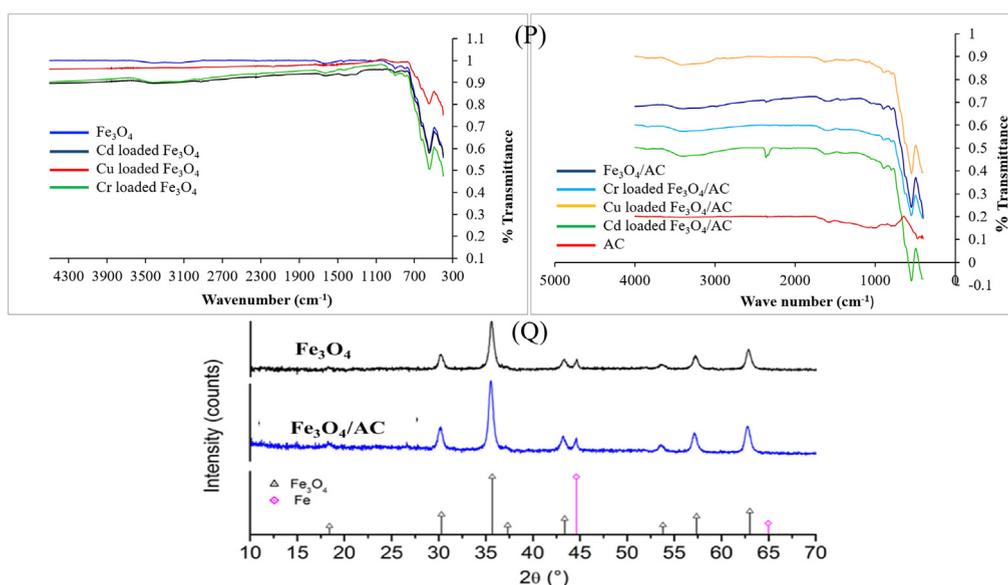


Fig. 1. ^PFT-IR spectra of Fe₃O₄, Cd, Cu and Cr loaded Fe₃O₄, Fe₃O₄/AC, Cr, Cu, Cd loaded Fe₃O₄/AC and AC, ^QPowder XRD of Fe₃O₄ and Fe₃O₄/AC.

Table 2
Average crystal size of Fe₃O₄ phases.

Nanoparticles	Fe ₃ O ₄ (220) nm	Fe ₃ O ₄ (311) nm	Fe ₃ O ₄ (400) nm	Fe ₃ O ₄ (511) nm
Fe ₃ O ₄	16	17	21	15
Fe ₃ O ₄ /AC	16	17	21	16

amine group. The peak around 1612.28 cm⁻¹ corresponds to -C=O stretching that may be attributed to lignin aromatic group. Similarly, in cadmium loaded Fe₃O₄/AC, the peaks shifted as compared to native nanoparticles (⁶Fig. 1). The additional peaks at 869.78 cm⁻¹ and 781.07 cm⁻¹ in Fe₃O₄/AC and Cr(VI) loaded Fe₃O₄/AC; 862.5 cm⁻¹ in Cu(II) loaded Fe₃O₄/AC; 875.57 cm⁻¹ and 767.57 cm⁻¹ in Cd(II) loaded Fe₃O₄/AC may be assigned to bending modes of aromatic compounds.

These changes indicated that the carboxyl, amino/hydroxyl groups present on the surface of native and metal loaded Fe₃O₄/AC are mainly involved in the adsorption of metal ions. The possible adsorption on these nanoparticles may be due to physical adsorption, complexation with functional groups [18,50], ion exchange [51], surface precipitation or chemical reaction with surface sites. The changes in FTIR spectra confirm the complexation of Cr(VI), Cu(II) and Cd(II) with functional groups present on the nanoparticles.

Comparison of powder X-ray diffraction (PXRD) patterns of Fe₃O₄ and Fe₃O₄/AC (²Fig. 1) samples revealed that the iron oxide nanoparticles in both samples are crystalline in nature and represent the cubic structure modification of Fe₃O₄ (magnetite). The characteristic diffraction peaks (with corresponding Miller indices) can be observed at 2θ of 30.18° (220), 35.54° (311), 43.21° (400), 54.00° (422), 57.16° (511) and 62.78° (440) respectively (Table 2). As all the observed peaks were assigned to the magnetite phase, no peaks for the potential hematite phase could be seen in either of the patterns. In addition, a very weak, broad diffraction hump at 2θ range of 23° was observed in case of Fe₃O₄/AC sample, confirming presence of activated carbon on the surfaces of magnetic nanoparticles [35]. The crystal size analysis with Scherrer equation indicated nearly the same crystal size of both the magnetite nanoparticles (~15–21 nm in diameter depending on the direction of the view of the crystal lattice).

The SEM micrographs of Fe₃O₄, Fe₃O₄/AC, Cr, Cu & Cd loaded Fe₃O₄ and Cr, Cu & Cd loaded Fe₃O₄/AC are shown in Fig. 2. SEM images give an idea about the shape and structure of the nanoparticles under study. AC has a tubular and porous structure (Fig. 5a & b) with smooth surface while images of Fe₃O₄ and Fe₃O₄/AC (Fig. 2a and e) reveal that the nanoparticles are agglomerated and stuck to each other thus, making the surface rough and coarse. The surface of the nanosorbents after loading with heavy metals (Fig. 2b, c, d, f, g and h) became smooth and shiny as visible in the images. The adsorption of heavy metals on the surface of nanoparticles was further confirmed by EDS. Detailed morphology and structure of the nanoparticles was further investigated by TEM.

As can be seen in the EDS spectra of Fe₃O₄ sample (Fig. 3a), it does not contain carbon and weight fraction of iron is 63.8% whereas in Fe₃O₄/AC (Fig. 3e), the weight fraction of carbon is 50.9% and iron content is only 18.4% confirmed by the sharp peaks of carbon and iron thus, indicating that the activated carbon content was significantly higher than Fe₃O₄ NPs. Moreover, EDS spectrum of Fe₃O₄/AC sample showed an additional peak that could be assigned to silicon that might have originated from the plant material. Partial images of b, c, d, f, g and h in Fig. 3 corresponds to the EDS spectra of Fe₃O₄ and Fe₃O₄/AC after loading with Cr, Cu and Cd respectively. The characteristic peaks of Cr, Cu and Cd in the spectra revealed that the metal ions bonded well with the surface of the nanoparticles.

TEM images of synthesized Fe₃O₄ and Fe₃O₄/AC nanoparticles along with the particle size distribution (in the inset i.e. Selected Area Diffraction Pattern) are given in Fig. 4a, b, c and d. The nanoparticles synthesized by co-precipitation method are nearly spherical in shape with an average particle size of 12.9 nm (Fe₃O₄) and 12.3 nm (Fe₃O₄/AC). The particle size of Fe₃O₄ and Fe₃O₄/AC was in the range of 7–19 nm and 9–18 nm respectively, thereby being consistent with XRD analysis (see earlier paragraph of same section).

The magnetic hysteresis loop of iron oxide nanoparticles (Fig. 6) was plotted between field strength (T) and ratio of magnetic moment to mass [J(A m² kg⁻¹)]. The saturation magnetization i.e. J_s [(A m² kg⁻¹)] that measures the maximum magnetic strength was found to be 59.3 and 52.2 A m²/kg respectively for Fe₃O₄ and Fe₃O₄/AC (Table 3). J_s values obtained for both the nanoparticles were lesser than the pure magnetite (Fe₃O₄) i.e. 92 A m² kg⁻¹ [52]. Although both the nanoparticles are quite similar in their magnetic properties but Fe₃O₄/AC has less saturation magnetization due to the presence of plant biomass in it (Table 3). However, this reduction in magnetization did not affect the attraction by external magnet as Fe₃O₄/AC was still strongly attracted by the external magnet. The coercivities [H_c (mT)] of Fe₃O₄ and Fe₃O₄/AC are 5.2 and 3.6 T respectively indicating that the nanoparticles are of ferromagnetic nature (Table 3). The remnant magnetization (J_r), a measure of the remaining magnetization when the driving field is dropped to zero is 5.3 and 4.0 (A m² kg⁻¹) for Fe₃O₄ and Fe₃O₄/AC respectively (Table 3). Thus, Fe₃O₄ and Fe₃O₄/AC with high saturation magnetization values can quickly respond to the external magnetic field thereby leading to their fast separation from the aqueous solution of heavy metal. The data indicated that both the specimens show similar hysteresis parameters (Table 3 and Fig. 6).

The TGA/DTG analysis was performed to identify the thermal behavior and stability of the nanoparticles in the nitrogen atmosphere. TGA was used to determine the thermal stability of Fe₃O₄ and Fe₃O₄/AC by monitoring the weight change that occurred when the samples were heated in an inert atmosphere of N₂. Fig. 7. showed the mass loss (TGA) and derivative mass loss (DTG) curves of Fe₃O₄ and Fe₃O₄/AC.

In Fig. 7, Fe₃O₄ showed two step degradation as indicated by the DTG peaks. The observed maximum weight loss occurred at first peak i.e. at around 65 °C which was attributed to the loss of moisture. The second peak at 270 °C in the temperature range of

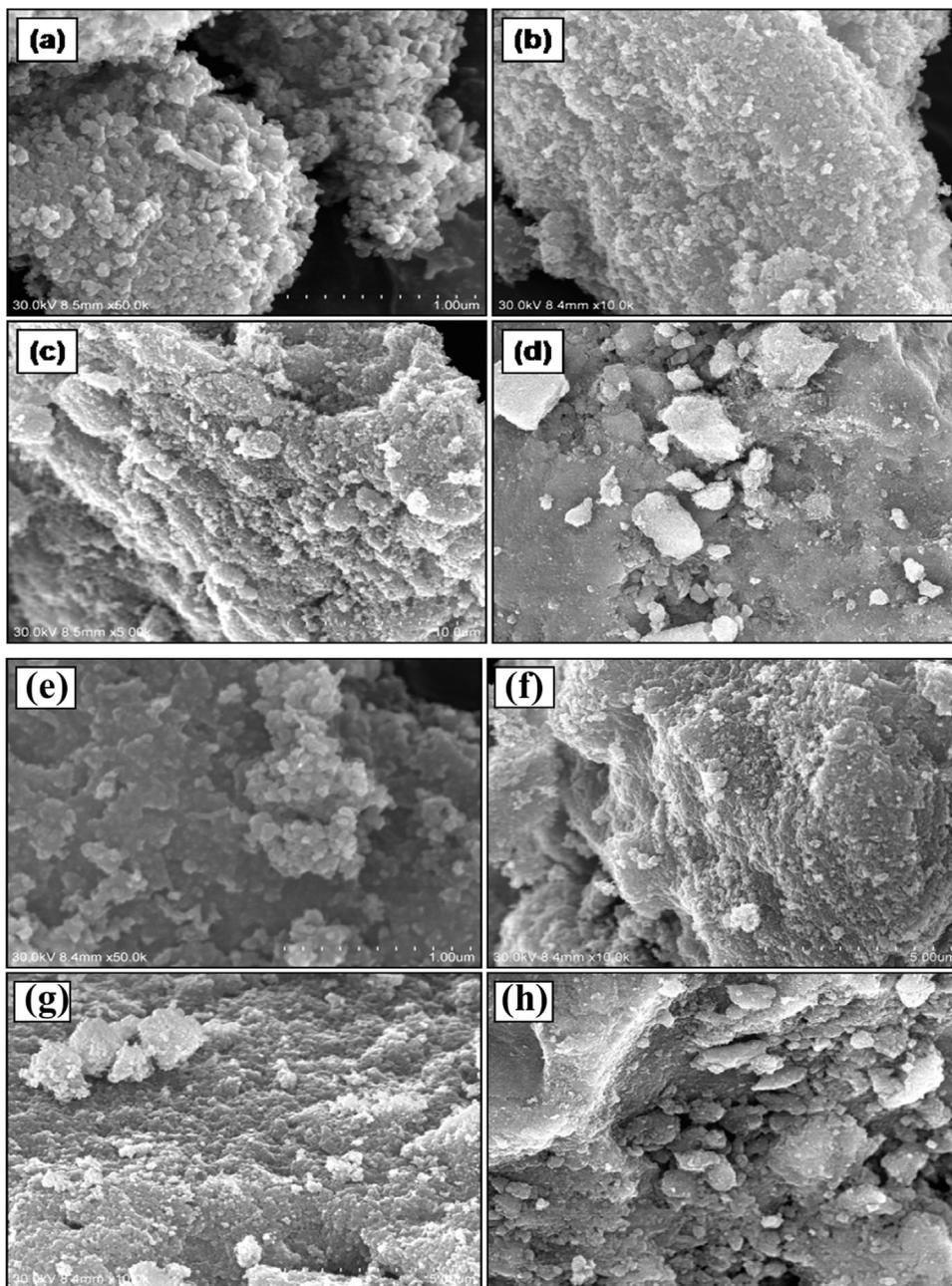


Fig. 2. SEM micrographs of (a) Fe_3O_4 (b) Cr loaded Fe_3O_4 (c) Cu loaded Fe_3O_4 (d) Cd loaded Fe_3O_4 (e) $\text{Fe}_3\text{O}_4/\text{AC}$ (f) Cr loaded $\text{Fe}_3\text{O}_4/\text{AC}$ (g) Cu loaded $\text{Fe}_3\text{O}_4/\text{AC}$ and (h) Cd loaded $\text{Fe}_3\text{O}_4/\text{AC}$.

175–400 °C, with a further weight loss of 1.7% corresponded to the removal of chemically bound moisture. Above 400 °C, only negligible change in mass (< 0.55%) was observed indicating that no further reactions occurred until 1000 °C thereby iron oxide being the sole residue with residual mass of 96% at the end of the degradation.

On the other hand, the degradation of $\text{Fe}_3\text{O}_4/\text{AC}$ occurred in four distinct stages as indicated by the DTG peaks. The first weight loss (below 175 °C) was mainly due to the loss of moisture. A second peak at around 276 °C with very low weight loss (within 175–387 °C) was found due to the thermal degradation of cellulose and hemicellulose [53]. Between 387 and 787 °C, a third peak with a loss of 8.4% was due to the devolatilization of more thermally stable heavy volatiles present in $\text{Fe}_3\text{O}_4/\text{AC}$ [54]. The fourth stage was from 787 to 969 °C, in which the slow weight loss was due to the pyrolysis of lignin in biomass [55–57]. At the end of temperature (999.2 °C), the final residual mass of 77.7% was identified which might be the representative of materials including iron oxide and some other carbonaceous residuals.

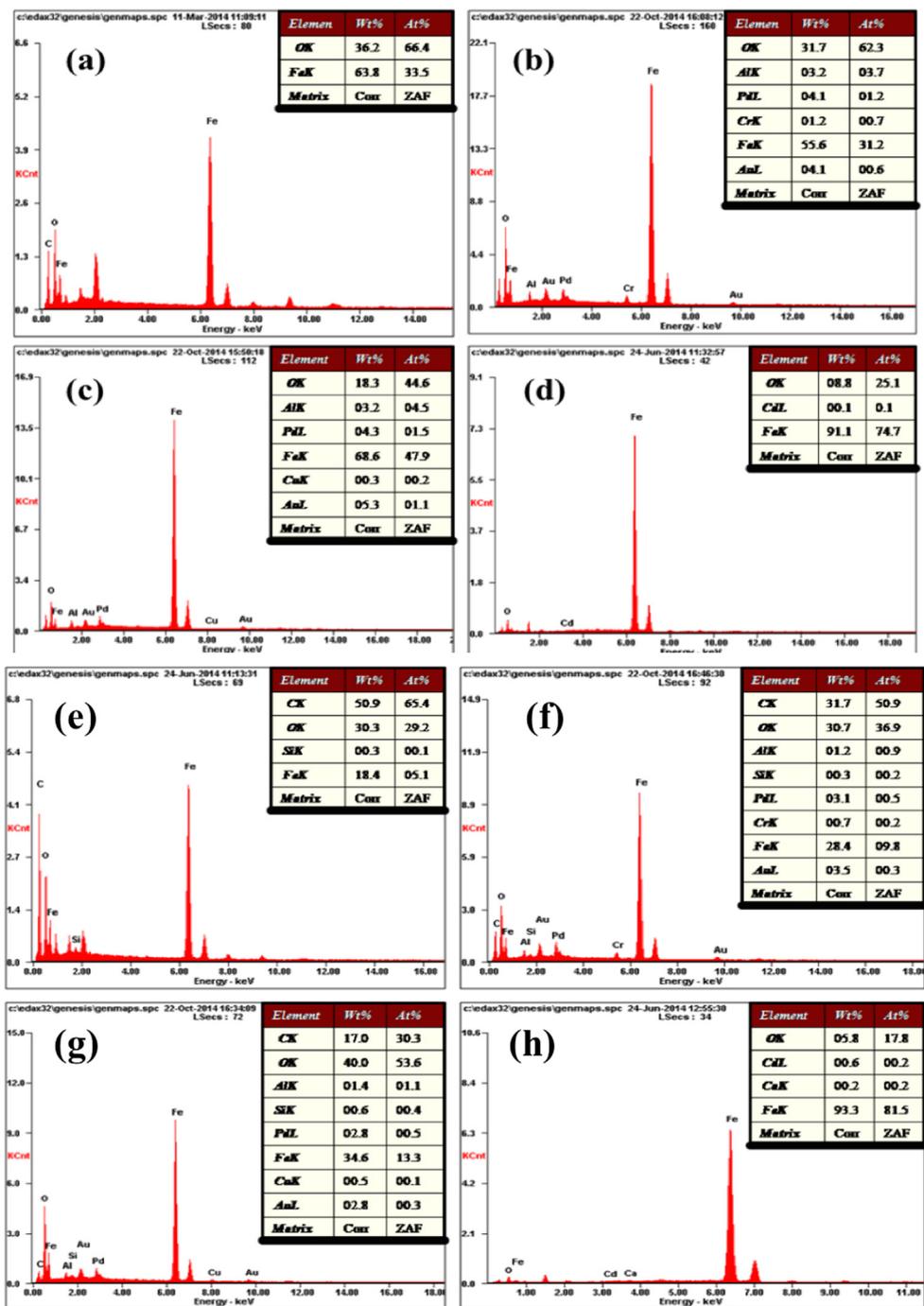


Fig. 3. EDS spectra of (a) Fe_3O_4 (b) Cr loaded Fe_3O_4 (c) Cu loaded Fe_3O_4 (d) Cd loaded Fe_3O_4 (e) Fe_3O_4/AC (f) Cr loaded Fe_3O_4/AC (g) Cu loaded Fe_3O_4/AC and (h) Cd loaded Fe_3O_4/AC and in the inset, elemental composition of Fe_3O_4 , metal loaded Fe_3O_4 , Fe_3O_4/AC and metal loaded Fe_3O_4/AC .

4.2. Batch adsorption studies

4.2.1. pH dependent studies

The effect of pH (Fig. 8a, b, c and d) on the adsorption of Cr(VI), Cu(II) and Cd(II) ions by Fe_3O_4 and Fe_3O_4/AC was studied in order to determine the optimum adsorption pH of the above said ions in the pH range of 2.0–7.0. While screening the pH values, all the other process variables such as initial metal ion concentration (50 mg L^{-1}), nanoparticle dose (50 mg/10 mL), temperature ($26 \pm 1 \text{ }^\circ\text{C}$), shaking speed (180 rpm) and contact time (3 h) were kept constant. A control experiment was also run (in the absence of

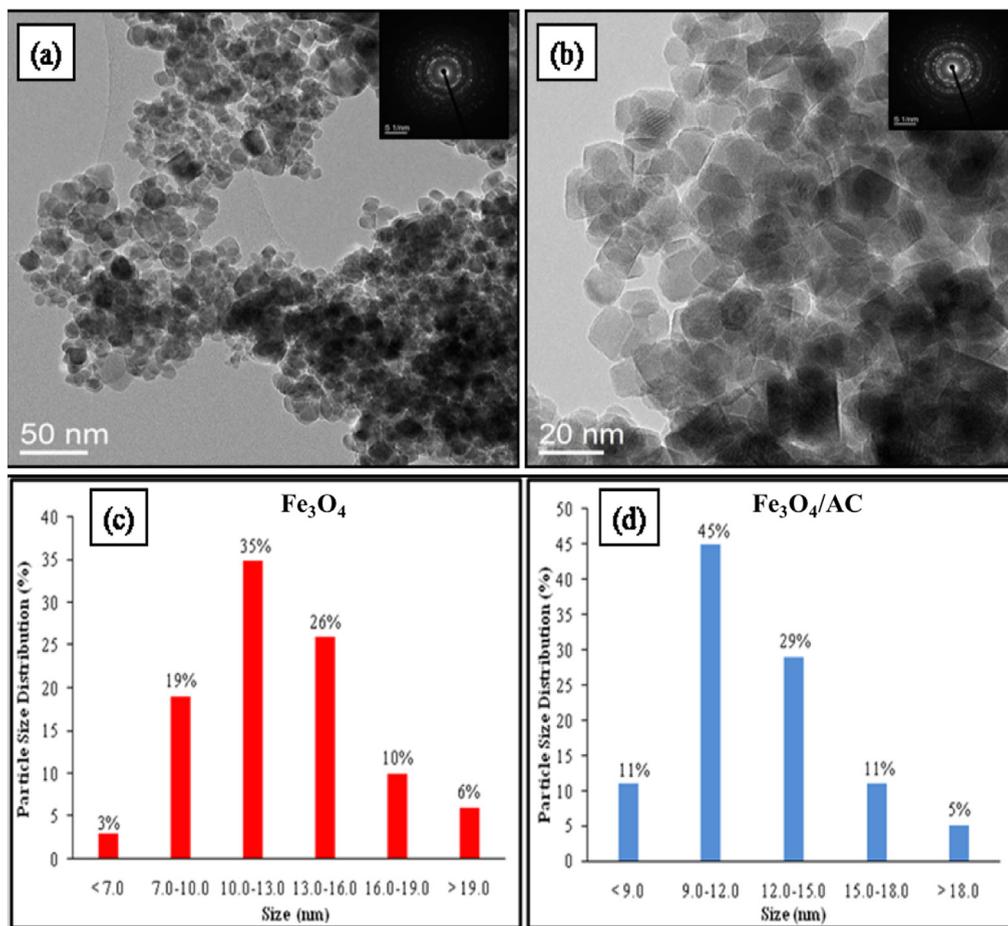


Fig. 4. TEM images of (a) Fe₃O₄ (b) Fe₃O₄/AC (c) Particle size distribution of Fe₃O₄ (d) Particle size distribution of Fe₃O₄/AC and in the inset, selected area diffraction pattern of Fe₃O₄ and Fe₃O₄/AC.

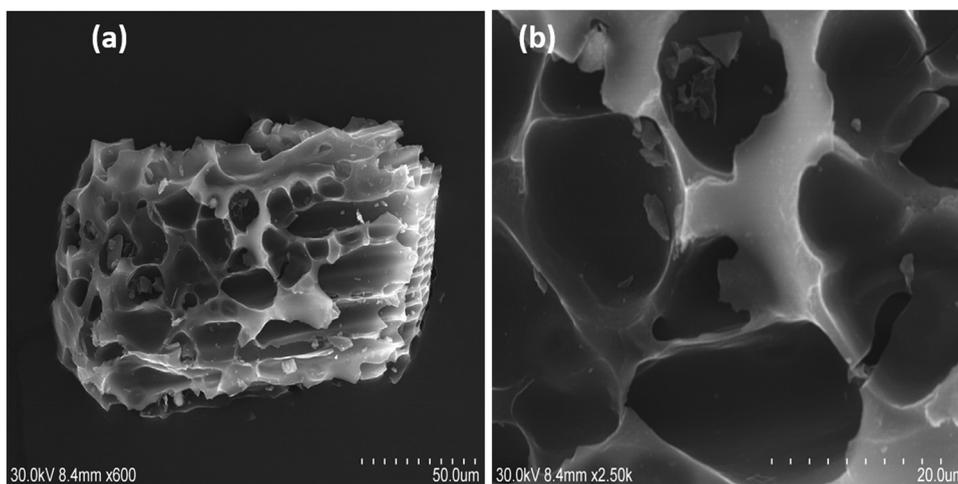


Fig. 5. SEM images of Sunflower Head Waste activated carbon (a) at 50.0 μm (b) at 20.0 μm.

nanoparticles) for the removal of Cr(VI), Cu(II) and Cd(II) to explore the effect of chemical precipitation (Fig. 8c). Performed control experiment revealed that there was no removal of Cr(VI) & Cd(II) up to pH 7.0 and Cu(II) up to pH 6.0 but when the pH was > 6.0 [for Cu(II)] and > 7.0 [for Cd(II) and Cr(VI)], all the three ions precipitated as hydroxides [Cr(OH)₂, Cu(OH)₂ and Cd(OH)₂] in the solution thus, leading to their complete removal. Keeping this in view, the adsorption studies were conducted in the pH range of

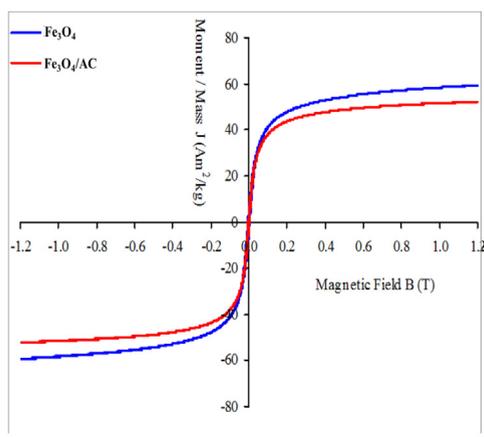


Fig. 6. Magnetic moment loop of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{AC}$.

Table 3

Magnetic properties of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{AC}$.

Nanoparticles	Coercivity [Hc (mT)]	Saturation magnetization [Js (Am^2/kg)]	Remanence (Am^2/kg)
Fe_3O_4	5.2	59.3	5.3
$\text{Fe}_3\text{O}_4/\text{AC}$	3.6	52.2	3.9

2.0–7.0 for Cr(VI) and Cd(II) and 2.0–6.0 for Cu(II), as Cu(II) precipitated at pH 7.0 and Cr(VI) and Cd(II) precipitated at pH 8.0.

Fig. 8a and b display that maximum removal of Cr(VI) was achieved at pH 2.0 and that of Cu(II) and Cd(II) was at pH 6.0. In case of Fe_3O_4 , it was observed that, Cr(VI) removal decreased (58.5–11.6%) as pH was increased from 2.0 to 7.0. Whereas Cu(II) and Cd(II) removal increased from 0% to 26.2% and 2.6% to 8.4% respectively when the pH was increased from 2.0 to 6.0. While the percentage removal decreased from 95.3% to 10.3% in case of Cr(VI), it increased from 0% to 85.6% and from 5.5% to 96.5% for Cu(II) and Cd(II) respectively when $\text{Fe}_3\text{O}_4/\text{AC}$ was used in the given pH range indicating higher removal efficiency of $\text{Fe}_3\text{O}_4/\text{AC}$ over Fe_3O_4 . It can be assumed that, it was the presence of different functional groups on the surface of activated carbon that led to the increased binding of more ions as suggested by Jain et al. [49].

One way to explain the mechanism of Cr(VI) removal is that, at lower pH, the surface of the nanoparticle is positively charged due to adsorption of H^+ ions from the aqueous solution. The chromium ions co-exist in different forms viz. HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, $\text{Cr}_3\text{O}_{10}^{2-}$, $\text{Cr}_4\text{O}_{13}^{2-}$ of which HCrO_4^- predominates in the pH range of 1.0–6.0 and chromate ions (CrO_4^{2-}) exists at pH > 6.0 [58]. This leads to an electrostatic attraction between the positively charged nanoparticles surface and negatively charged chromate ions thus, leading to an increase in the removal at lower pH (pH = 2.0) (Scheme 1). The decrease in the removal at higher pH may be due to competition between chromate (CrO_4^{2-}) and hydroxyl ions (OH^-) for adsorption on the surface of the nanoparticles. So, the most probable mechanism for adsorption of chromium on the surface of nanoparticles is electrostatic attraction/repulsion [59]. The adsorption was highest at pH 2.0 for Cr(VI) on both the nanoparticle specimens and therefore, pH 2.0 was chosen as the optimum pH for forthcoming experiments.

The adsorption of Cu(II) and Cd(II) was less at lower pH but increased with the increase in pH. This behavior may be due to the reason that: lower pH leads to an abundance of hydronium ions (H_3O^+) in the solution that causes competition between hydronium ions and Cu(II) or Cd(II) ions (copper and cadmium ions are present as Cu^{2+} , $\text{Cu}(\text{OH})^+$, Cd^{2+} and $\text{Cd}(\text{OH})^+$ at lower pH) for adsorption onto nanoparticles thereby lowering the overall adsorption efficiency of these metal ions at lower pH [60]. Similar kind of results were reported by Ianos et al. [61] who synthesized iron oxide/carbon nanocomposite for the removal of acid blue 129 dyes from simulated wastewater. They found that the adsorption capacity of acid blue at pH = 2.3 was 4 mg g^{-1} .

On the other hand, at higher pH values, the functional groups present on the surface of the nanoparticles like carboxylic acid, hydroxyls, phenol are deprotonated thus creating negative sites on the nanoparticles. This leads to an electrostatic attraction between these negatively charged adsorption sites and positively charged Cu^{2+} and Cd^{2+} ions thus, increasing their adsorption [62]. Since the adsorption was highest at pH 6.0 for both Cu^{2+} and Cd^{2+} , it was chosen as the optimum pH for both these ions.

The point – zero charge pH (pH_{pzc}) plays an important role while studying the effect of pH (Fig. 8d). At pH < pH_{pzc} , the surface of the nanoparticles is positively charged and at pH > pH_{pzc} , the surface of the nanoparticles is negatively charged. Because the pH_{pzc} values were found to be 5.2 and 7.04 respectively for Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{AC}$, it can be stated that the surface of these nanoparticles was positively charged below pH_{pzc} 5.2 and 7.04. This confirmed that the hydrogen chromate ions were adsorbed through electrostatic attraction and Cu^{2+} and Cd^{2+} were repelled due to electrostatic repulsion between the two. While the surface of the nanoparticles was negatively charged above pH_{pzc} 5.2 and 7.04, this led to the electrostatic repulsion between the nanoparticles surface and chromate ions and electrostatic attraction between nanoparticles surface and Cu^{2+} and Cd^{2+} ions.

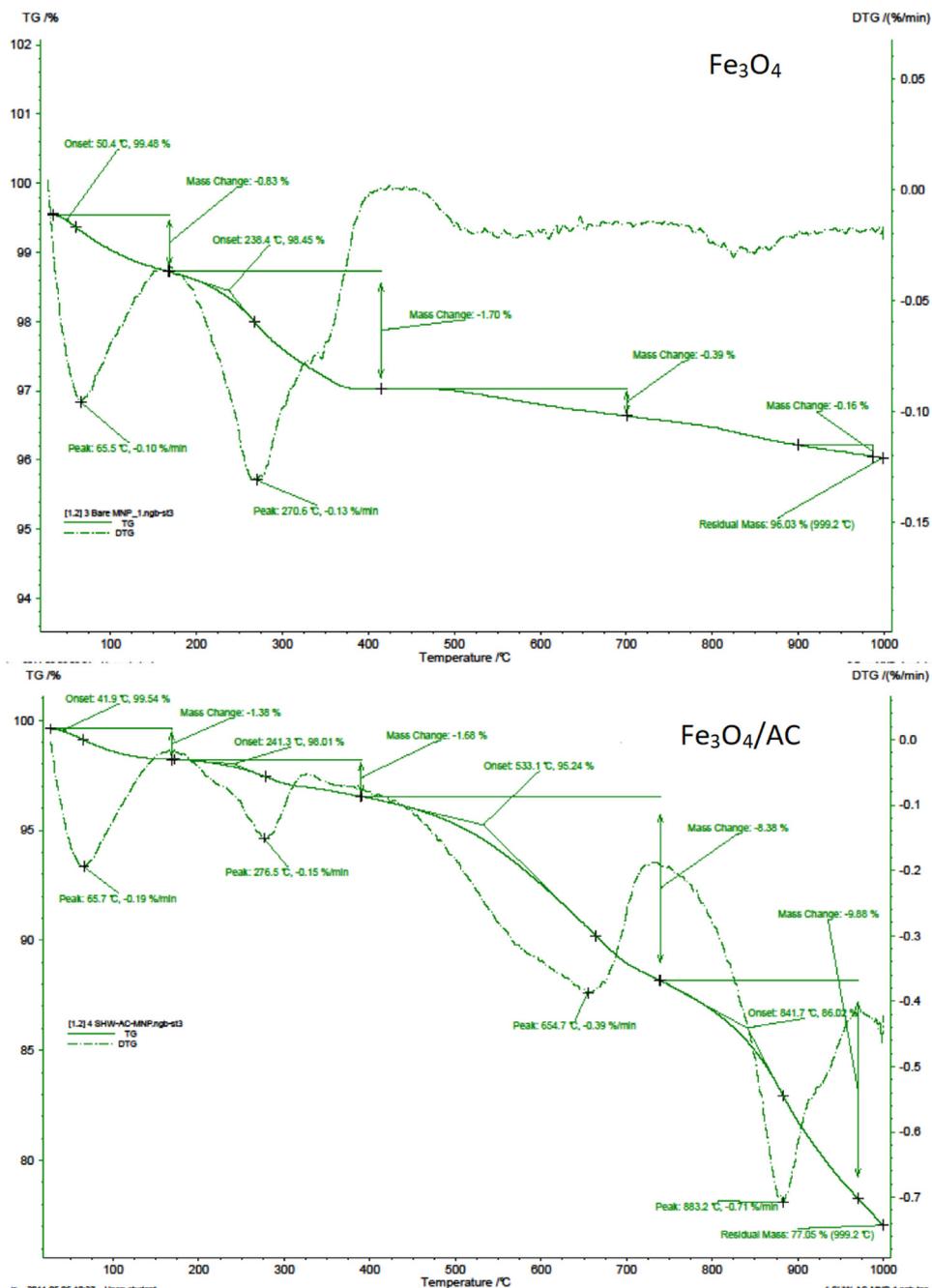


Fig. 7. TGA/DTG profile of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{AC}$.

4.2.2. Metal ion concentration dependent studies

The effect of initial metal ion concentration by Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{AC}$ at concentration varying from 10 to 500 mg L^{-1} keeping all other process variables constant (see details in pH dependent studies) is depicted in Fig. 8(e and f). The figures revealed that the metal removal by both the nanoparticles decreased as the metal ion concentration in the solution was increased from 10 to 500 mg L^{-1} in the solution. The metal removal efficiency decreased from 74.7% to 20.8% for Cr(VI), 60.0–10.5% for Cu(II) and 27.4–0 for Cd(II) in case of Fe_3O_4 and 98.9–31.7% for Cr(VI), 99.9–12.5% for Cu(II) and 99.9–8.1% for Cd(II) by $\text{Fe}_3\text{O}_4/\text{AC}$. Our results are in agreement with Kera et al. [63] who fabricated magnetic polypyrrole (PPy)–polyaniline (PANI)/iron oxide (Fe_3O_4) nanocomposite for the removal of Cr(VI). This nanocomposite was efficient in removing 99% of Cr(VI) from aqueous solution at pH 2.0, initial metal ion concentration of 100 mg L^{-1} and a nanocomposite dose of 0.05 g.

However, overall adsorption capacity of all the three metal ions increased on both the nanoparticles with an increase in concentration. It increased from 0.4 to 5.2 mg g^{-1} for Cr(VI), 0.3–2.6 mg g^{-1} for Cu(II) but no adsorption capacity for Cd(II) in case of

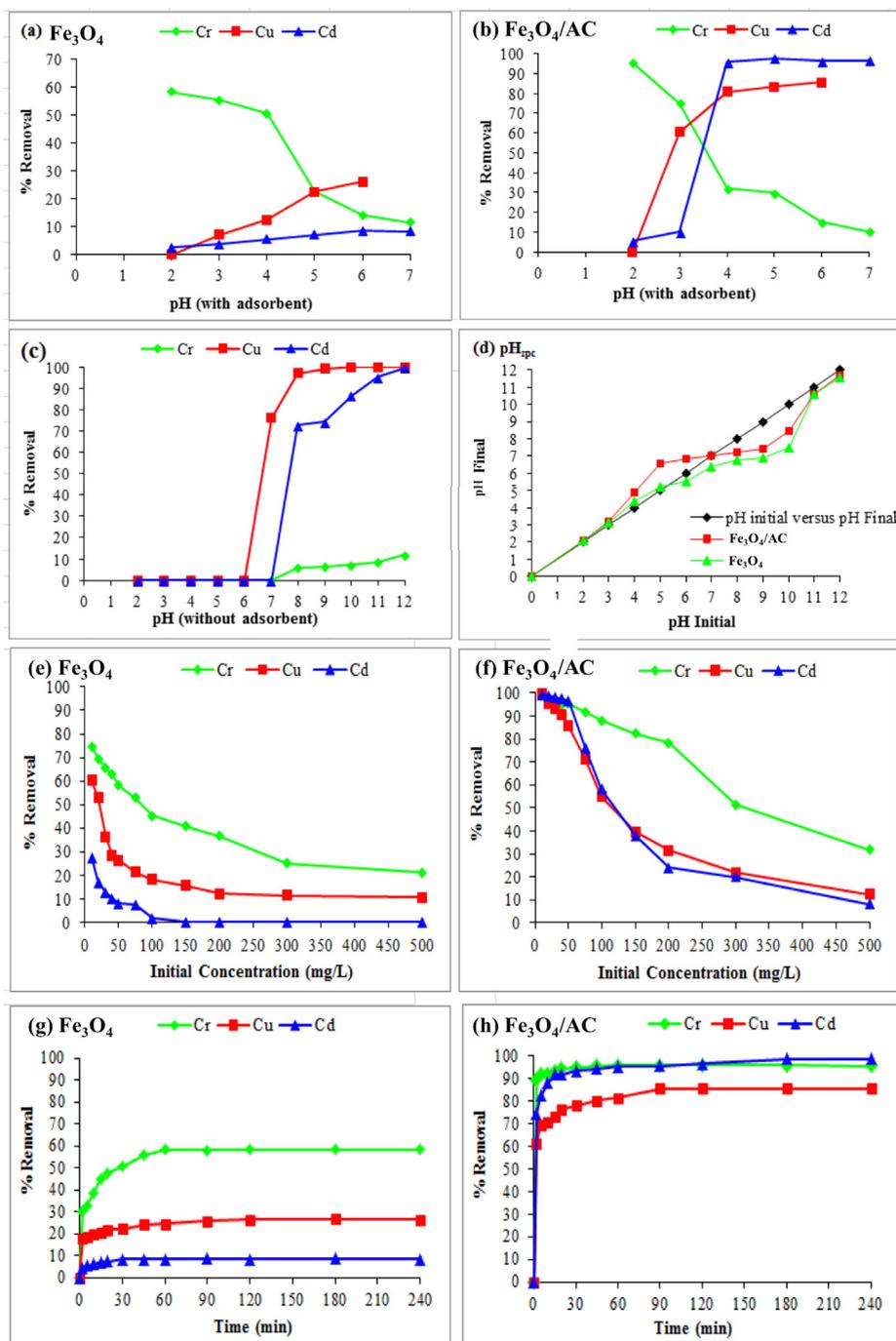
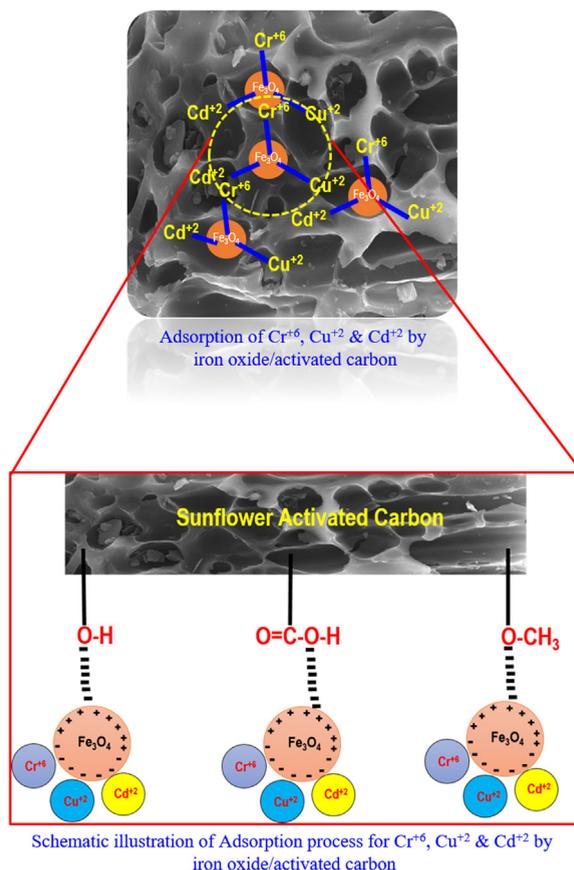


Fig. 8. ^{a,b,c,d}Effect of pH on Cr(VI), Cu(II) and Cd(II) removal by Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{AC}$, without nanoparticles and pH_{pzc} , ^{e,f}Effect of initial metal ion concentration on Cr(VI), Cu(II) and Cd(II) removal by Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{AC}$, ^{g,h}Effect of contact time on Cr(VI), Cu(II) and Cd(II) removal by Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{AC}$.

Fe_3O_4 whereas a similar trend was observed by $\text{Fe}_3\text{O}_4/\text{AC}$ i.e. 0.5–8.0 mg g^{-1} for Cr(VI), 0.5–3.0 mg g^{-1} for Cu(II) and 0.5–2.0 mg g^{-1} for Cd(II). This could be explained on the basis that the ionic radii (0.95 Å) of Cd(II) was high among the three ions. Moreover, Fe_3O_4 doesn't contain any of the functional groups present on $\text{Fe}_3\text{O}_4/\text{AC}$. Thus, Cd(II) couldn't have access to the pores of the adsorbent, so it couldn't be removed.

The decrease in removal efficiency with an increase in metal ion concentration may be due to the fact that as the concentration of metal ion increases, increasingly more surface sites are covered and hence at higher metal ion concentration, the adsorption capacity of the nanoparticles get exhausted due to non-availability of free binding sites thus, resulting in a decrease in the overall removal



Scheme 1. . Adsorption mechanism for the removal of Cr(VI), Cu(II) and Cd(II) by $\text{Fe}_3\text{O}_4/\text{AC}$ nanocomposite

efficiency [64]. It is therefore evident that, at low concentration ranges, the percentage of adsorption is high because of the availability of more active sites on the surface of nanoparticles. The increase in adsorption capacity can be explained on the basis that, an increase in initial metal ion concentration led to an increase in diffusion of Cr(VI), Cu(II) and Cd(II) ions from the solution phase to the surface of the nanoparticles due to an increase in the driving force of the metal ions which lead to the collisions between metal ions and the nanoparticles surface thus, resulting in an increase in adsorption capacity [22].

4.2.3. Contact time dependent studies

Next, the effect of contact time on the removal of Cr(VI), Cu(II) and Cd(II) by Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{AC}$ was investigated to determine the optimum time taken to attain the equilibrium (Fig. 8g and h). The adsorption experiments were carried out by varying the contact time between 2 and 240 min keeping all other process variables constant. Fig. 8g and h depicts that, removal percentage increased with an increase in the contact time. The equilibrium was achieved within 60, 120 and 30 min for Cr(VI), Cu(II) and Cd(II) respectively by Fe_3O_4 . The removal efficiency increased from 30.4% to 58.3% for Cr(VI), 17.7% to 26.4% for Cu(II) and 4.4% to 8.2% for Cd(II) by Fe_3O_4 after which it became constant and further removal of these metal ions was not observed.

While in case of $\text{Fe}_3\text{O}_4/\text{AC}$, removal of Cr(VI) reached 95.5% within 45 min from the start of the experiment after which it became constant with no further removal. Similarly, 85.5% Cu(II) was removed within 90 min, whereas 96.5% Cd(II) was removed within 120 min. In case of Cr(VI) and Cd(II) ions, high removal efficiencies were achieved at early stage of the experiment, as 89.4% and 74.5% removal reached within first 2.0 min, after which there was gradual increase till equilibrium time. Despite the short equilibrium time, the experiments were run for 240 min, in order to ensure complete adsorption of ions from the solution. Similar kind of results were reported by Wannahari et al. [23] who combined activated carbon generated from sugarcane bagasse with magnetic iron oxide nanoparticles for the removal of Cu(II) ions. They interpreted that 77% of Cu(II) was removed at pH 4.0 within 60 min at 50 °C and would solve the problem of waste disposal.

It was observed that, the rate of Cr(VI), Cu(II) and Cd(II) binding with Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{AC}$ was faster at initial stages, which slowed down with the progress of time and remained almost constant after an optimum period or attainment of equilibrium. This may be attributed to the quick uptake of ions onto the large surface area of nanoparticles with an increase in the contact time, but after equilibrium was achieved, the removal efficiency of the metal ions slowed down as the free surface of the nanoparticles decreased due to the increased coverage by the bound ions [65]. Overall, the trend for both the nanoparticles is same i.e. with the increase in contact time; there is an increase in adsorption percentage.

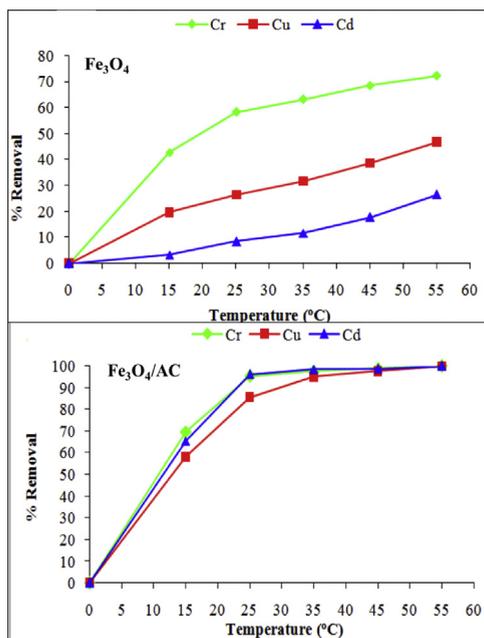


Fig. 9. Effect of temperature on Cr(VI), Cu(II) and Cd(II) removal by Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{AC}$.

4.2.4. Temperature dependent studies

The effect of temperature on the removal of metal ions by Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{AC}$ was studied by varying the temperature in the range of 288–328 K again keeping all other process variables constant. The results revealed that the adsorption of ions increased with an increase in temperature (Fig. 9). The adsorption efficiency increased from 42.7% to 72.3% for Cr(VI), 19% to 46.8% for Cu(II) and 3.3% to 24.4% for Cd(II) by Fe_3O_4 . While, in case of $\text{Fe}_3\text{O}_4/\text{AC}$, the increase in adsorption efficiency was observed from 69.7% to 99.9% for Cr(VI), 58.2% to 99.8% for Cu(II) and 65.4% to 99.8% for Cd(II) respectively. Aigbe et al. [66] reported that the poly-pyrrolle iron oxide magnetic nanocomposite prepared by them was useful in removing Cr(VI) ions from wastewater. The authors found that the highest Cr(VI) removal was 99.2% at following process conditions: magnetic field = 18.99 mT, Cr(VI) concentration = 50 mg L^{-1} , pH = 2.0, contact time = 150 min and temperature = 25 °C.

The results indicated that the maximum removal percentage was recorded at 328 K thus suggesting that the adsorption process was endothermic in nature. This may be due to the fact that, increase in temperature leads to an increase in mobility of the ions which in turn increases the interaction between the ions and the nanoparticles surface [67]. Although highest removal percentage was obtained at 328 K but 298 K was chosen as the optimum temperature for all the experiments as this temperature is suitable for practical application under field conditions.

On the basis of the results obtained from Sections 4.2.1 to 4.2.4, a table (Table 4) has been prepared mentioning the conditions required for the highest removal efficiency of synthesized nanocomposites for removal of heavy metals Cr(VI), Cu(II) and Cd(II).

4.2.5. Thermodynamic studies

Thermodynamic studies help in predicting whether the adsorption mechanism is physical or chemical in nature. The thermodynamic parameters viz. standard Gibb's free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) for the removal of Cr(VI) Cu(II), Cd(II) by Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{AC}$ were calculated by applying following equations [68]:

$$\Delta G^\circ = -RT \ln K \quad (4)$$

$$\Delta H^\circ = \left[\frac{RT_1 T_2}{(T_2 - T_1)} \right] \ln \left(\frac{K_2}{K_1} \right) \quad (5)$$

Table 4

Conditions for the highest removal efficiency of synthesized nanocomposite for the removal of Cr(VI), Cu(II) and Cd(II).

Heavy metals	pH	Temperature	Initial concentration	Contact time	
				Fe_3O_4	$\text{Fe}_3\text{O}_4/\text{AC}$
Cr(VI)	2.0	$25 \pm 1^\circ\text{C}$	50 mg L^{-1}	60 min	45 min
Cu(II)	6.0	$25 \pm 1^\circ\text{C}$	50 mg L^{-1}	120 min	90 min
Cd(II)	6.0	$25 \pm 1^\circ\text{C}$	50 mg L^{-1}	120 min	90 min

Table 5Thermodynamic parameters for adsorption of Cr(VI), Cu(II), Cd(II) by Fe₃O₄ at different temperatures.

Temp (K)	ΔG° (J mol ⁻¹)	ΔH° (J mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
Thermodynamic parameters for adsorption of Cr(VI) onto Fe ₃ O ₄			
288	7875.3	44,602.6	127.5
298	6602.0	16,011.6	31.6
308	6286.3	19,598.4	43.2
318	5854.0	15,427.3	30.1
328	5553.0	0	-16.9
Thermodynamic parameters for adsorption of Cu(II) onto Fe ₃ O ₄			
288	11,026.4	49,458.9	133.4
298	9692.3	0	-32.5
308	10,017.5	33,017.3	74.7
318	9269.3	24,947.3	49.3
328	8775.5	0	-26.8
Thermodynamic parameters for adsorption of Cd(II) onto Fe ₃ O ₄			
288	15,260.7	69,459.6	188.2
298	13,341.6	28,060.8	49.4
308	12,871.7	41,345.9	92.4
318	11,965.3	43,814.8	100.2
328	10,965.3	0	-33.4

$$\Delta S^\circ = \left(\frac{\Delta H^\circ - \Delta G^\circ}{T} \right) \quad (6)$$

$$K = \left(\frac{qe}{Ce} \right) \quad (7)$$

where R (8.314 J mol⁻¹ K⁻¹) is the universal gas constant, K is the equilibrium constant at temperature T, T is the absolute temperature (K), C_e (mg L⁻¹) is the equilibrium concentration and q_e is the amount of Cr(VI) Cu(II), Cd(II) adsorbed on the surface of Fe₃O₄ and Fe₃O₄/AC. Tables 5 and 6 gives the thermodynamic parameters for adsorption of Cr(VI) Cu(II), Cd(II) adsorbed on the surface of Fe₃O₄ and Fe₃O₄/AC at different temperatures.

Tables 5 and 6 reveals that the negative value of ΔG° signifies that the adsorption process is feasible and spontaneous in nature. This is in agreement with the results obtained from the Langmuir separation factor R_L where the R_L values were found between 0 and 1 i.e. (0 < R_L < 1) and the Freundlich exponent n was also greater than 1. With the increase in temperature, the value of ΔH° decreased indicating that the increase in temperature was favorable for the adsorption process [69]. The positive value of ΔH° signifies that the adsorption process is endothermic and irreversible in nature. The positive value of ΔS° signifies that the adsorption process is a combination of the two simple processes i.e. Gibb's free energy (ΔG°) and standard enthalpy (ΔH°). Moreover, the positive values of ΔS° also indicated that the adsorbent surface had the affinity for Cr(VI), Cu(II) and Cd(II) ions and the degrees of disorder and randomness was high at the solid solution interface [70].

Table 6Thermodynamic parameters for adsorption of Cr(VI), Cu(II), Cd(II) by Fe₃O₄/AC at different temperatures.

Temp (K)	ΔG° (J mol ⁻¹)	ΔH° (J mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
Thermodynamic parameters for adsorption of Cr(VI) onto Fe ₃ O ₄ /AC			
288	5178.4	154,838.3	519.7
298	-239.3	49,906.2	168.3
308	-1710.1	67,994.6	226.3
318	-3973.9	208,731.1	668.9
328	-10,665.3	0	32.5
Thermodynamic parameters for adsorption of Cu(II) onto Fe ₃ O ₄ /AC			
288	6378.8	103,820.2	338.3
298	3005.3	87,908.2	284.9
308	130.6	58,548.6	189.7
318	-1765.6	221,045.1	700.7
328	-8772.2	0.0	26.7
Thermodynamic parameters for adsorption of Cd(II) onto Fe ₃ O ₄ /AC			
288	5648.5	185,092.5	623.1
298	-582.2	67,762.6	229.3
308	-2873.9	17,100.4	64.9
318	-3524.3	223,473.2	713.8
328	-10,665.3	0.0	32.5

Table 7Langmuir, Freundlich and Redlich- Peterson isotherm parameters for the removal of Cr(VI), Cu(II) and Cd(II) by Fe₃O₄ and Fe₃O₄/AC.

	Fe ₃ O ₄			Fe ₃ O ₄ /AC		
	Chromium	Copper	Cadmium	Chromium	Copper	Cadmium
Langmuir Parameters						
Q _o (mg g ⁻¹)	5.5	2.7	0.09	8.06	3.2	2.15
b (L mg ⁻¹)	0.02	0.008	0.07	0.17	0.33	0.11
R ²	0.9660	0.8179	0.7331	0.9994	0.9998	0.9750
Freundlich Parameters						
K _f (mg g ⁻¹)	0.29	0.16	0.03	1.44	1.4	1.4
n (L mg ⁻¹)	1.9	2.4	1.71	2.7	6.7	7.1
R ²	0.9774	0.9483	0.5995	0.9336	0.9274	0.6194
Redlich- Peterson Parameters						
K _{RP} (L/g)	1	2	1	0.5	2	4
α _{RP} (L/mg)	2.9	0.93	27.9	13.5	0.9290	0.99
β	0.52	0.93	0.06	0.07	0.9285	1.00
R ²	0.9814	0.9996	0.8442	0.5165	0.9996	0.9974

4.2.6. Adsorption isotherms

Batch adsorption data was described using Langmuir, Freundlich and Redlich-Peterson models. Langmuir adsorption model assumes that an adsorbent contains fixed number of binding sites. All the binding sites have same affinity for the adsorbate. Each site adsorbs only one molecule thus, forming a single monolayer. The linear form of Langmuir model and its separation factor R_L is expressed in Eqs. (8) and (9):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (8)$$

$$R_L = \frac{1}{1 + bC_i} \quad (9)$$

where, Q_o (mg g⁻¹) is the maximum Langmuir adsorption capacity and b (L mg⁻¹) is the Langmuir constant related to free energy. The Langmuir constants Q_o and b were calculated from the slope and intercept of the Langmuir plot of C_e versus C_e/q_e (Table 4). The value of Q_o was highest for Cr(VI) by both the nanoparticles i.e 8.06 mg g⁻¹ for Cr(VI), 3.2 mg g⁻¹ for Cu(II) and 2.15 mg g⁻¹ for Cd(II) by Fe₃O₄/AC while it was 5.5 mg g⁻¹ for Cr(VI), 2.7 mg g⁻¹ for Cu(II) and 0.09 mg g⁻¹ for Cd(II) by Fe₃O₄. R² (Regression coefficient) values were very high, being almost unity for Cr(VI), Cu(II) and Cd(II) by Fe₃O₄/AC as compared to Fe₃O₄ [0.9660 for Cr(VI), 0.8179 for Cu(II) and 0.7331 for Cd(II) (Table 8)]. The values of Langmuir R² for Cd(II) by Fe₃O₄; Cr(VI), Cu(II) and Cd(II) by Fe₃O₄/AC were higher than Freundlich model thus, indicating that Langmuir model fitted the data in good congruence, thereby indicating monolayer adsorption. The tea waste biomass loaded with nano-Fe₃O₄ particles (TW/Fe₃O₄) composite was synthesized by Fan et al. [71] for the removal of Cr(VI) from aqueous solution. The maximum Langmuir adsorption capacity was found to be 62.1 mg g⁻¹ by the authors at pH 2.0, contact time 10 h and temperature 25 °C.

The Langmuir separation factor (R_L) which is a dimensionless constant indicates whether the adsorption process is favorable or not. R_L was calculated for the nanoparticles under study using Eq. (5) where b (L mg⁻¹) and C_i (mg L⁻¹) have already been explained. The criterion for favorable adsorption was chosen on the basis of R_L values. If R_L values are greater than 1.0, adsorption is unfavorable, if R_L values are equal to 1.0, adsorption is linear, if R_L values are between 0 and 1, adsorption is favorable and if R_L

Table 8R_L values for the removal of Cr(VI), Cu(II) and Cd(II) by Fe₃O₄ and Fe₃O₄/AC.

I. Conc. (mg L ⁻¹)	Fe ₃ O ₄			Fe ₃ O ₄ /AC		
	Chromium	Copper	Cadmium	Chromium	Copper	Cadmium
10	0.854	0.919	0.595	0.365	0.232	0.575
20	0.746	0.850	0.423	0.224	0.131	0.729
30	0.662	0.791	0.329	0.161	0.091	0.391
40	0.594	0.740	0.268	0.126	0.070	0.267
50	0.540	0.694	0.227	0.103	0.057	0.203
75	0.439	0.602	0.164	0.071	0.039	0.127
100	0.370	0.532	0.128	0.054	0.029	0.092
150	0.281	0.431	0.089	0.037	0.020	0.060
200	0.227	0.362	0.068	0.028	0.015	0.044
300	0.163	0.275	0.047	0.019	0.010	0.029
500	0.105	0.185	0.029	0.011	0.006	0.017

values are equal to 0, adsorption is irreversible. For the present system, the R_L values were between 0 and 1 (0.01–0.919) for Cr(VI), Cu(II) and Cd(II) by both the nanoparticles indicating favorable adsorption process (Table 8).

Freundlich adsorption model assumes that adsorbents have a heterogeneous surface having sites with different adsorption potential. It also assumes that stronger binding sites are occupied first and the binding strength decreases with the increasing degree of occupation. The Freundlich adsorption model in its linear form is given in Eq. (10):

$$\log_{10} q_e = \log_{10}(K_f) + \left(\frac{1}{n}\right) \log_{10}(C_e) \quad (10)$$

where K_f (mg g^{-1}) is the Freundlich constant indicating adsorption capacity, n (L mg^{-1}) is the adsorption intensity that is the measure of the change in affinity of the adsorbate with the change in adsorption density. The Freundlich constants K_f and n were calculated from the slope and intercept of the plot of C_e versus $\log_{10} q_e$ (Table 7). When $n = 1$, Freundlich isotherm becomes linear and indicates that all the sites on the nanoparticles have equal affinity for the adsorbate. The adsorption intensity, $n > 1$, indicates that affinity decreases with the increase in adsorption density and $n < 1$ indicates poor adsorption. The adsorption intensity (n) values were found to be greater than 1 for all the three metal ions under study by Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{AC}$ (Table 7). The values of (R^2) in Freundlich model for Cr(VI) and Cu(II) by Fe_3O_4 viz. 0.9774 and 0.9483 were higher as compared to Langmuir model thus, indicating that Freundlich model fitted the data well confirming multilayer adsorption.

The Redlich–Peterson isotherm given by Redlich and Peterson is a combination of Langmuir and Freundlich isotherms. The numerator is from Langmuir isotherm and denominator has both Langmuir and Freundlich forms. This model includes three parameters into an empirical equation. Therefore, it can be applied to both homogenous and heterogeneous systems. This model does not follow ideal monolayer adsorption. The Redlich–Peterson model in its linear form is expressed in Eq. (11) [72]:

$$\ln\left(\frac{K_{RP} C_e - 1}{q_e}\right) = \ln(\alpha_{RP}) + \beta \ln(C_e) \quad (11)$$

where K_{RP} (L g^{-1}) and α_{RP} (L mg^{-1}) are the Redlich–Peterson constants and β is the exponent which lies between 0 and 1. C_e (mg L^{-1}) and q_e (mg g^{-1}) are same as mentioned in Eqs. (2) and (3) respectively in the Langmuir model. When the exponent β approaches zero, Eq. (7) converts to Henry's law equation i.e. R–P equation approaches to Freundlich model at higher concentration and when exponent β approaches one, Eq. (9) converts to Langmuir form. The value of β lied between 0 and 1 indicating favorable adsorption (Table 7).

4.2.7. Adsorption kinetics

The rate of reaction and reaction pathways are described by adsorption kinetics which depends upon the physical and chemical characteristics of the adsorbent. The adsorption kinetics was described using three models viz. pseudo-first order, pseudo-second order and intraparticle diffusion model. The adsorption in solid–liquid system was described by Pseudo-first-order kinetic model [Lagergren's equation, Eq. (12)]. This model assumes that one metal ion is sorbed onto one sorption site on the surface of the adsorbent:

$$\log_{10} (q_e - q_t) = \log_{10} q_e - \frac{k_1}{2.303} t \quad (12)$$

where q_e is the adsorption capacity at equilibrium time and q_t (mg g^{-1}) is the adsorption capacity at time t (min), and K_1 (min^{-1}) is the equilibrium rate constant for pseudo-first-order model. The value of K_1 is derived from the slope of the linear plots of $\log(q_e - q_t)$ versus time (min). The values of q_e (experimental) (mg g^{-1}), q_e (calculated) (mg g^{-1}), K_1 (min^{-1}) and R^2 for Cr(VI), Cu(II) and Cd(II)

Table 9

Pseudo-1st-order, Pseudo-2nd-order and Intraparticle Diffusion kinetic parameters for the removal of Cr(VI), Cu(II) and Cd(II) by Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{AC}$.

	Fe_3O_4			$\text{Fe}_3\text{O}_4/\text{AC}$		
	Chromium	Copper	Cadmium	Chromium	Copper	Cadmium
Pseudo-1st-order Kinetic parameters						
q_e (exp) (mg g^{-1})	2.38	0.74	0.25	2.39	2.14	2.47
q_e (cal) (mg g^{-1})	0.14	0.36	0.12	0.31	0.74	0.38
K_1 (min^{-1})	0.0987	0.0223	0.0119	0.106	0.047	0.02
R^2	0.5166	0.4238	0.4609	0.692	0.5481	0.6295
Pseudo-2nd-order Kinetic parameters						
q_e (exp) (mg g^{-1})	2.38	0.74	0.25	2.39	2.14	2.47
q_e (cal) (mg g^{-1})	2.37	0.75	0.25	2.39	2.16	2.47
K_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	3.076	0.2387	0.669	2.21	0.23	0.28
R^2	1	0.9983	0.9947	1	0.9998	0.9998
Intraparticle Diffusion Parameters						
K_{ID} (mg/g min)	0.0613	0.79	0.011	0.645	0.0792	0.0819
BL	1.7834	1.278	0.1125	1.7534	1.278	1.5831
R^2	0.1951	0.4312	0.6326	0.2172	0.4312	0.3472

by both the nanosorbents are given in Table 9. The table indicates that the values of regression coefficient (R^2) for pseudo-first order model are poor and the calculated q_e values are not near to experimental q_e values thus, indicating a poor fit of this model to our data. Therefore, the adsorption of Cr(VI), Cu(II) and Cd(II) by Fe_3O_4 and Fe_3O_4/AC was examined using pseudo-second-order model.

The pseudo-second-order model (Eq. (13)) assumes that, one metal ion is sorbed onto two sorption sites on the surface of the adsorbent. This model has been used for analyzing chemisorption kinetics from liquid solutions. K_2 ($g\ mg^{-1}\ min^{-1}$) is the equilibrium rate constant and K_2q_e is the initial adsorption rate ($mg\ g^{-1}\ min^{-1}$) for pseudo-second-order model. The values of $1/K_2q_e^2$ and $1/q_e$ are derived from the intercept and slope of the linear plots of t/q_t versus time (min), which leads to calculation of the values of K_2 and q_e (calculated):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (13)$$

The values of q_e (experimental) ($mg\ g^{-1}$), q_e (calculated) ($mg\ g^{-1}$), K_2 ($g\ mg^{-1}\ min^{-1}$) and R^2 for Cr(VI), Cu(II) and Cd(II) by Fe_3O_4 and Fe_3O_4/AC are given in Table 9. The table indicates that the values of regression coefficient are near to unity for Cr(VI), Cu(II) and Cd(II) by both the nanosorbents and values of q_e (experimental) and q_e (calculated) are almost near to each other thus, revealing that pseudo-second-order model fits the data well as compared to pseudo-first-order model.

Weber-Morris model (1963) is employed to further analyze the adsorption kinetics and to assess the importance of diffusion during the adsorption process. This model (Eq. (14)) describes the movement of ions from bulk solution to the solid phase. It assumes that the adsorption process occurs in two steps. The first straight portion depicts macropore diffusion (i.e. diffusion of heavy metals from the solution to the exterior surface of the nanosorbent, which can be regarded as the external diffusion) and the second one represents micropore diffusion (diffusion from the surface of the nanosorbent into the pores):

$$q_t = K_{id} t^{0.5} + BL \quad (14)$$

where q_t is same as above, K_{id} is the intra-particle diffusion rate constant ($mg\ g^{-1}\ min^{-1/2}$) which can be obtained from the slope of the straight line (slope of the plots between q_t and $t^{1/2}$) and BL is the thickness of the boundary layer obtained from the intercept of the plots between q_t and time (min). The values of K_{id} and BL are given in Table 9. Larger the value of BL, greater is the boundary layer effect. If intra-particle diffusion occurs, then q_t against $t^{1/2}$ will be linear and the line will pass through the origin. But, in our case, the line didn't pass through the origin that means some other process is also involved in the adsorption. The intra-particle diffusion rate constants calculated from this model are not zero which indicates that the adsorption process may not be controlled by intra-particle diffusion model [73].

4.2.8. Desorption studies

The regeneration and reuse of adsorbents has become economically important because of the high cost incurred in wastewater purification systems. Thus, it becomes necessary to check the reusability of the adsorbent for successive sorption-desorption cycles. For desorption experiments, Cr, Cu and Cd-loaded nanoparticles were first washed three times with deionized water in order to remove any loosely attached metal ion from their surface. They were then dried in hot air oven at $80\ ^\circ C$ for 2 h. Desorption was done using 0.1 M HCl (volume of desorbing agent = 10 mL) for 60 min in 15 mL disposable, capped tubes at $26 \pm 1\ ^\circ C$ and agitation speed of 180 rpm on a rotary shaker. Hydrochloric acid is commonly used for eluting metal ions from adsorbents because of its frequent use in industry, relatively low cost and solubility of metal ions in it [74]. The nanoparticles were separated by a strong magnet and the supernatant was collected for measuring of metal concentration in the solution. Residual concentration of metal ions in the solution was determined in a similar way as in the adsorption experiments. The reusability of the nanoparticles was tested by following the above adsorption-desorption process up to four cycles for Cr(VI), Cu(II) and Cd(II) ions (Fig. 10). The metal recovery was calculated by the following Eq. (15):

$$\% \text{ Desorption Efficiency} = \frac{\text{Amount of metal ion desorbed}}{\text{Amount of metal ion sorbed}} \times 100 \quad (15)$$

Fig. 10 depicted that desorption efficiency decreased with each sorption-desorption cycle. Desorption efficiency of Cu(II) and Cd(II) was found to be fairly high for first cycle i.e. 80.6% and 83.9% respectively but quiet low for Cr(VI) i.e. 21.3% by Fe_3O_4/AC which reduced gradually with the proceeding cycles.

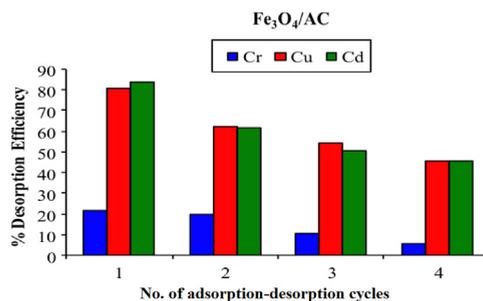


Fig. 10. Desorption of Cr(VI), Cu(II) and Cd(II) from Fe_3O_4/AC by HCl.

Table 10Comparison of adsorption capacity of Fe₃O₄/AC with other adsorbents.

Adsorbents	Adsorption capacity (mg/g)	pH	Temp.	Heavy Metals			References
				Cr(VI)	Cu(II)	Cd(II)	
Fe ₃ O ₄ @APS@AA-co-CA MNPs	29.6	5.5	25 °C	–	–	–	[75]
Carboxymethyl Cyclodextrin (CM-CD) polymer modified Fe ₃ O ₄ nanoparticles	27.7	5.5	25 °C	–	–	–	[76]
Iron oxide nanoparticles	18.59	5.5	25 °C	–	–	–	[77]
Iron oxide nanoparticles	17.6	5.1	27 °C	–	Cu(II)	–	[78]
Magnetic nano-particles CuFe ₂ O ₄	17.54	6.0	45 °C	–	–	Cd(II)	[79]
Fe ₃ O ₄ /SC	15	6.5	27 °C	–	–	Cd(II)	[80]
RHC-mag-CN	16	3.0	25 °C	Cr(VI)	–	–	[81]
Amino functionalized magnetic nanosorbent	12.43	5.0	25 °C	–	Cu(II)	–	[82]
Amino functionalized magnetic nanosorbent	11.24	2.0	25 °C	Cr(VI)	–	–	[82]
MCCAC	9.67	2.0	27 °C	Cr(VI)	–	–	[83]
Magnetic oak bark char	7.40	5.0	25 °C	–	–	Cd(II)	[62]
Biofunctional magnetic beads	6.73	1.0	28 °C	Cr(VI)	–	–	[84]
Iron oxide NPs embedded in orange peel pith	5.37	1.0	–	Cr(VI)	–	–	[85]
Magnetic oak wood char	2.87	5.0	25 °C	–	–	Cd(II)	[62]
Fe ₃ O ₄ /AC	4.4	2.0	25 °C	Cr(VI)	–	–	This study
Fe ₃ O ₄ /AC	2.7	6.0	25 °C	–	Cu(II)	–	This study
Fe ₃ O ₄ /AC	2.9	6.0	25 °C	–	–	Cd(II)	This study

While, the desorption efficiency was high for Cu(II) and Cd(II), it was substantially low for Cr(VI). This may be due to the reason that Cr(VI) might be chemically bonded with the Fe₃O₄/AC thus, restricting its desorption. It was found that 0.1 M HCl was quite effective in desorbing Cr(VI), Cu(II) and Cd(II) ions from the surface of nanosorbents. The obtained results verified that the Fe₃O₄ nanoparticles synthesized with co-precipitation process can be recovered effectively for the re-adsorption of the metal ions. The regeneration of Fe₃O₄/AC also indicated that adsorption of Cr(VI), Cu(II) and Cd(II) on to the Fe₃O₄/AC was a reversible process and the nanoparticles were quiet stable even after four adsorption-desorption cycles.

4.2.9. Comparison of adsorption capacity with other adsorbents

The maximum adsorption capacity of Fe₃O₄/AC nanocomposite for the removal of Cr(VI), Cu(II) and Cd(II) was compared with other adsorbents reported in the literature and the values are given in Table 10. It is clear from Table 10, that the adsorption capacity of Fe₃O₄/AC nanocomposite is comparable with other nanomaterials suggesting that, it is effective in removing Cr(VI), Cu(II) and Cd(II) from aqueous solutions [62,75–85].

5. Conclusion

In this article, the adsorption potential of Fe₃O₄ and Fe₃O₄/AC nanoparticles was investigated for the removal of Cr(VI), Cu(II) and Cd(II) ions. TEM analysis revealed that the synthesized nanoparticles were spherical in nature with an average particle size of 12.9 nm for Fe₃O₄ and 12.3 nm for Fe₃O₄/AC. The XRD analysis of Fe₃O₄ and Fe₃O₄/AC confirmed the presence of magnetite phase exhibiting average crystal size similar to that indicated by the TEM analysis. The maximum magnetic strength was found to be 59.3 and 52.2 A m² kg⁻¹ respectively of Fe₃O₄ and Fe₃O₄/AC. The optimum adsorption pH was found to be 2.0 for Cr(VI) and 6.0 for Cu(II) and Cd(II) respectively. The removal efficiency of nanoparticles decreased with an increase in the concentration i.e. 74.7–20.8% for Cr(VI), 60.0–10.5% for Cu(II) and 27.4–0 for Cd(II) by Fe₃O₄ and 98.9–31.7% for Cr(VI), 99.9–12.5% for Cu(II) and 99.9–8.1% for Cd(II) by Fe₃O₄/AC. The adsorption efficiency for Cr(VI) and Cd(II) was high in the beginning of the experiments as indicated by 89.4% and 74.5% removal in the first 2.0 min. The conditions for the highest removal efficiency of synthesized nanocomposite for the removal of Cr(VI), Cu(II) and Cd(II) were pH = 2.0 and 6.0, temperature = 25 ± 1 °C, initial metal ion concentration = 50 mg L⁻¹ contact time = 60 and 45 min for Cr(VI) by Fe₃O₄ and Fe₃O₄/AC, 120 and 90 min for Cu(II) and Cd(II) by Fe₃O₄ and Fe₃O₄/AC. The maximum Langmuir adsorption capacity was 8.06 mg g⁻¹ for Cr(VI), 3.2 mg g⁻¹ for Cu(II) and 2.15 mg g⁻¹ for Cd(II) by Fe₃O₄/AC while it was 5.5 mg g⁻¹ for Cr(VI), 2.7 mg g⁻¹ for Cu(II) and 0.09 mg g⁻¹ for Cd(II) by Fe₃O₄. The desorption efficiency was fairly high in first cycle i.e. 80% and 83% for Cu(II) and Cd(II) which decreased gradually till the fourth cycle. In case of Cr(VI), substantially lower desorption efficiency of 23.2% was determined.

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