



AUIQ Complementary Biological System

ISSN: 3007-973X

Journal homepage:

<https://acbs.alayen.edu.iq>



Volume 2 | Issue 1

Article 6

Removal of Cr(VI) from Aqueous Solution Using Magnetic Activated Carbon Prepared from Waste Shell of *Marigold Flower Straw*: Kinetics, Isotherm and Mechanism Studies

Shanmukha Rao Metta

Department of Chemistry, Gandhi Institute of Engineering and Technology University, Gunupur, Odisha-765022, India

Uttam Kumar Sahu

Department of Chemistry, Gandhi Institute of Engineering and Technology University, Gunupur, Odisha-765022, India

Follow this and additional works at: <https://acbs.alayen.edu.iq/journal>



Part of the [Biology Commons](#), [Biotechnology Commons](#), and the [Medicine and Health Sciences Commons](#)

Recommended Citation

Metta, Shanmukha Rao and Sahu, Uttam Kumar (2025), Removal of Cr(VI) from Aqueous Solution Using Magnetic Activated Carbon Prepared from Waste Shell of *Marigold Flower Straw*: Kinetics, Isotherm and Mechanism Studies, *AUIQ Complementary Biological System*: Vol. 2: Iss. 1, 77-89.

DOI: <https://doi.org/10.70176/3007-973X.1025>

Available at: <https://acbs.alayen.edu.iq/journal/vol2/iss1/6>



ORIGINAL STUDY

Removal of Cr(VI) from Aqueous Solution Using Magnetic Activated Carbon Prepared from Waste Shell of *Marigold Flower Straw*: Kinetics, Isotherm and Mechanism Studies

Shanmukha Rao Metta, Uttam Kumar Sahu^{ID} *

Department of Chemistry, Gandhi Institute of Engineering and Technology University, Gunupur, Odisha-765022, India

ABSTRACT

When Cr(VI) was released from industrial waste into water bodies harms aquatic ecosystems and poses risks to human well-being. To reduce risks, it's crucial to lower Cr(VI) levels through the sustainable process. In order to extract Cr(VI) from a liquid, the magnetic activated carbon adsorbent was created for the current investigation. H_3PO_4 was utilised as an activating agent in the thermal procedure to prepare activated carbon from marigold flower straw for the first time. The marigold flower straw activated carbon (MFSAC) was further decorated with Fe_3O_4 nanoparticles ($\text{Fe}_3\text{O}_4/\text{MFSAC}$) in the reflux process. The complete analysis of the MFSAC and $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite properties was carried out utilizing X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), BET (Brunauer-Emmett-Teller) and zero-point charge (pH_{IEP}) to get information about the morphology, functional group, crystallinity, surface area, and surface charge respectively. At an initial concentration of 20 mg/L, a pH of 3, a contact time of 40 minutes, and an adsorbent dose of 2 g, around 99% of Cr(VI) was eliminated. The Langmuir isotherm showed that the $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite could adsorb 8.76 mg/g. The pseudo-second-order kinetic model had the best-fitting R^2 values, which were 0.99. On the surface of the $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite, electrostatic attraction and porosity adsorption were the main mechanisms for Cr(VI) adsorption. Therefore, in wastewater treatment, the $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite functions as a possible adsorbent.

Keywords: Marigold flower straw, Chromium, Fe_3O_4 , Activated carbon, Adsorption

1. Introduction

In current century, the heavy metal pollution is the most dangerous global environmental issues. Chromium (Cr) is among the most dangerous pollutants made of heavy metals produced by industries such as textiles, steel manufacturing, metal finishing, leather tanning, and electroplating. There are several chemical types of Cr, and its oxidation states range from 0 to 6; nevertheless, the greater levels of Cr oxidation are particularly notable because of their toxic characteristics [1]. There are only two types

of chromium that are stable enough in an aquatic environment: trivalent and hexavalent [2]. Because of its mobility, high solubility, oxidation potential, tiny size, and effective mobility in biological systems (cell membranes), Cr(VI) is considered to be more than 100 times more dangerous than Cr(III) [2]. It is claimed that Cr(VI) possesses mutagenic and carcinogenic properties [3]. The capacity of Cr(VI) to solvate at various pH levels and penetrate cell membranes, whether prokaryotic or eukaryotic, has heightened its potential impact on DNA mutations via the build-up of reactive oxygen species (ROS) [4].

Received 6 February 2025; revised 24 February 2025; accepted 24 February 2025.
Available online 8 March 2025

* Corresponding author.

E-mail address: sahuuttam02@gmail.com, uttamsahu@giet.edu (U. K. Sahu).

<https://doi.org/10.70176/3007-973X.1025>

3007-973X/© 2025 Al-Ayen Iraqi University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

As a result, eliminating Cr(VI) from aqueous solution is crucial.

Cr(VI) has been reduced or eliminated from aquatic environments using a variety of methods, such as electrocoagulation and precipitation [5], reverse osmosis [6], ultrafiltration [7], adsorption [8], biological and microbial reduction [9], photocatalysis [10], liquid membrane filtration [11], ion exchange [12]. Adsorption is regarded as one of these techniques that works well, straightforward, and as well as a quite inexpensive method for Cr(VI) remove [13]. Additionally, adsorption can not only manage pollutants while simultaneously recovering and reusing them in industrial operations [14]. In recent days iron oxides show great potential in order to remove Cr(VI) and are commonly used in water purification due to their ecological safety, affordability, and comparatively strong stability [15, 16]. Furthermore, the magnetic properties of Fe_3O_4 nanoparticles, which facilitate facile separation, and their straightforward manufacturing have attracted a lot of interest [17]. However, researchers also have observed that iron oxides have a small surface area due to their magnetic nature which often restricts their work to batch experiments [18]. Therefore, to support iron oxide nanoparticles some base materials are required which possess high surface area.

Currently, natural polymers like chitosan [19], cellulose [20], alginate [21], guar gum [22, 23], gum Arabic [24] and activated carbon [25, 26], are utilized to wastewater in order to eliminate Cr(VI). It is possible for a complex to develop with various metal ions thanks to these biodegradable substances. Adding the right functional group to these compounds by esterification [27], oxidation processes [28], or crosslinking techniques [29] can improve this characteristic. Activated carbon possesses a high surface area, mesoporous in nature, environmentally friendly, minimal diffusion length and ultimately can act as a very good base materials to support iron oxide nanoparticles [30]. Recently, agricultural waste materials like coconut shell [25], tea waste [1], jute fibre [17], etc. used in manufacture of activated carbon and have gotten very good results. Cr(VI) has also been eliminated using single-activated carbon; however, issues with chemical stability and reusability have been note [31]. Therefore, it is expected that adding Fe_3O_4 to activated carbon will improve the adsorbents' capacity to separate using an external magnetic field from aqueous solution in addition to strengthening their chemical stability [32, 33].

Marigold flower is widely used in India for worship, decoration and other cultural activities, hence a tons of flower has been generated every day and going

to dustbin without any use. Here, marigold flower straw is used as an activating agent in a thermal procedure for making activated carbon, and then Fe_3O_4 nanoparticles are generated over the activated carbon surface using the reflux method to boost the removal efficiency. The Fe_3O_4 /MFSAC composite's adsorption properties are completely unknown, and its suitability for treating Cr(VI) wastewater has not yet been assessed. Thus, the primary goals of this analysis were to: (a) employ experimental methods to characterise the Fe_3O_4 /MFSAC composite; (b) optimise the parameter for maximal removal of Cr(VI); and (c) apply kinetic and isothermal models to determine the Cr(VI) adsorption process.

2. Materials and methods

2.1. Materials

The marigold flower straw was gathered for one month from the dustbin of GIET University temple, Gunupur, Rayagada, Odisha-765022, India. The straw was washed several times before oven drying for two days at 90 °C. The straw was then cut into several pieces and finely ground to powder form of mesh size 150 microns. It was put in an airtight bottle after being cleansed with distilled water for later usage and oven-dried for two days at 90 °C. Phosphoric acid (H_3PO_4), sodium hydroxide (NaOH), conc. hydrochloric acid (HCl) and ammonia solution (NH_4OH) were brought from Loba Chemicals, India. Hexahydrate and tetrahydrate of iron chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, respectively) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) are purchased from Sigma-Aldrich chemicals. The potassium dichromate was purchased from Himedia Chemical, Mumbai.

2.2. Preparation of activated carbon

Concentrated phosphoric acid was applied to the produced marigold flower straw powder in a weight ratio of 1:4 at room temperature for 24 hours. In oven set to 120°C was used to dry the mixture for 2 days. After that, the final product was cleaned to get rid of any remaining residue acid using double-distilled hot water. The material that was acquired was forwarded to a hot air muffle furnace under nitrogen atmosphere. At 250° C, the material activation was complete with heating scan of 15° C/min for a time duration 2 h. Then, the obtained activated carbon was stored in an airtight bottle known as marigold flower straw activated carbon (MFSAC).

2.3. Preparation of iron oxide decorated activated carbon

Here, a straightforward reflux technique was used to decorate the iron oxide nanoparticles on the MFSAC surface. 50 mL of double-distilled water was mixed with 2.67 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 5.35 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were mixed in the ratio 1:2 with 50 mL double distilled water and rapidly stirred for 30 min [34]. After that, 1 g of the MFSAC that was prepared earlier was mixed up with the solution vigorously for 15 min. After that, add 25 mL of 25% NH_4OH to the mixture above and stir vigorously for 90 min at 85°C in a nitrogen atmosphere. After allowing the mixture in the reaction to cool, hot water was used for washing several times to remove the untreated ammonium hydroxide up to pH 7. Finally, the magnetic composite was for 24 h at 85°C in an oven and named as $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite stored in a bottle for adsorption studies.

2.4. Batch adsorption studies

A 1000 mg/L Cr(VI) stock solution was first made by mixing 2.828 g of potassium dichromate with 1 L of double-distilled water. The necessary concentration was attained by diluting the stock solution. To determine the ideal percentage removal, isotherm, and kinetics investigations, the effects of the adsorbent dosage (0.5 to 3 g), starting concentration (10 to 80 mg/L), duration (5 to 60 min), and pH (3 to 11) were reviewed in batch process. Here, 150 mL polylab plastic bottles holding 50 mL of Cr(VI) solution were used for the batch studies. The pH of the solution was maintained using a solution of sodium hydroxide (NaOH) and hydrochloric acid (HCl). Following adsorption, the materials were magnetically separated, and a UV-visible spectrophotometer was used to detect the quantity of residual Cr(VI) at 440 nm. The adsorbent's adsorption capacity and the percentage of Cr(VI) removal are calculated using Eqs. (1) and (2) [35, 36];

$$R(\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

$$q_e = \frac{C_o - C_e}{W} \times V \quad (2)$$

Where q_e and R is equal to the quantity of Cr(VI) on the composite surface (mg/g) and the rate of elimination (%); W and V stand for weight of composite (g) and volume of Cr(VI) solution (L), respectively. The concentrations at starting and equilibrium periods are C_o and C_e , respectively, expressed in mg/L.

2.5. Characterization techniques

MFSAC and $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite elemental composition and surface morphology were detected using a scanning electron microscope (FESEM) equipped with field emission and energy dispersive spectra (EDX) (JSM-7800, Japan). The phases and crystal structure of MFSAC and $\text{Fe}_3\text{O}_4/\text{MFSAC}$ have been ascertained by X-ray diffraction (XRD) pattern analysis using the RIGAKU JAPAN/ULTIMA-IV equipment, respectively. Using a Perkin Elmer RX-I FTIR analyser, the functional groups of the MFSAC and $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite—the active binding sites were discovered. A Quantachrome surface area analyser was utilised to ascertain the MFSAC and $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite's BET surface area, pore volume, and pore diameter. The Zeta size Nano ZEN3690 manufactured in Malvern, UK, was used to calculate the surface charge of $\text{Fe}_3\text{O}_4/\text{MFSAC}$. The UV-visible spectrophotometer (UV-Shimadzu 2450) was used to measure the amount of Cr(VI) in the 1,5-diphenylcarbazide (DPC) method.

3. Result and discussion

3.1. Characterization of the adsorbents

Fig. 1 shows the morphologies and elementals of MFSAC and $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite. As seen in Fig. 1a, MFSAC shows a porous arrangement consisting of plenty of micropores and macropores, which were spread all over the surface. MFSAC has a larger number of porous cavities which will provide an active number of binding sites and ultimately favourable for adsorption. Fig. 1b presents that MFSAC has only C and O with a ratio of 66.66:33.34. The distribution of Fe_3O_4 nanoparticles on MFSAC surfaces is seen in Fig. 1c. Fe_3O_4 nanoparticles covered the entire surface area of the MFSAC, and the small spherical aggregate of nanoparticles beautifully covered the surface. Fig. 1d shows the elemental composition of $\text{Fe}_3\text{O}_4/\text{MFSAC}$, which showed that Fe was present together with C and O. This confirmed that iron oxide nanoparticles had formed on the MFSAC surface. The Cr(VI) adsorbed $\text{Fe}_3\text{O}_4/\text{MFSAC}$ surface is shown in Fig. 1e. After adsorption, the surface of $\text{Fe}_3\text{O}_4/\text{MFSAC}$ was completely changed after adsorption, it's become smooth and compact. As can be observed, the particles were widely distributed and did not agglomerate, suggesting that their surface had been adsorbed with Cr(VI) metal ions. In Fig. 1f, Cr(VI) is seen alongside C, O, and Fe, indicating that Cr(VI) has been adsorbed on the $\text{Fe}_3\text{O}_4/\text{MFSAC}$ surface.

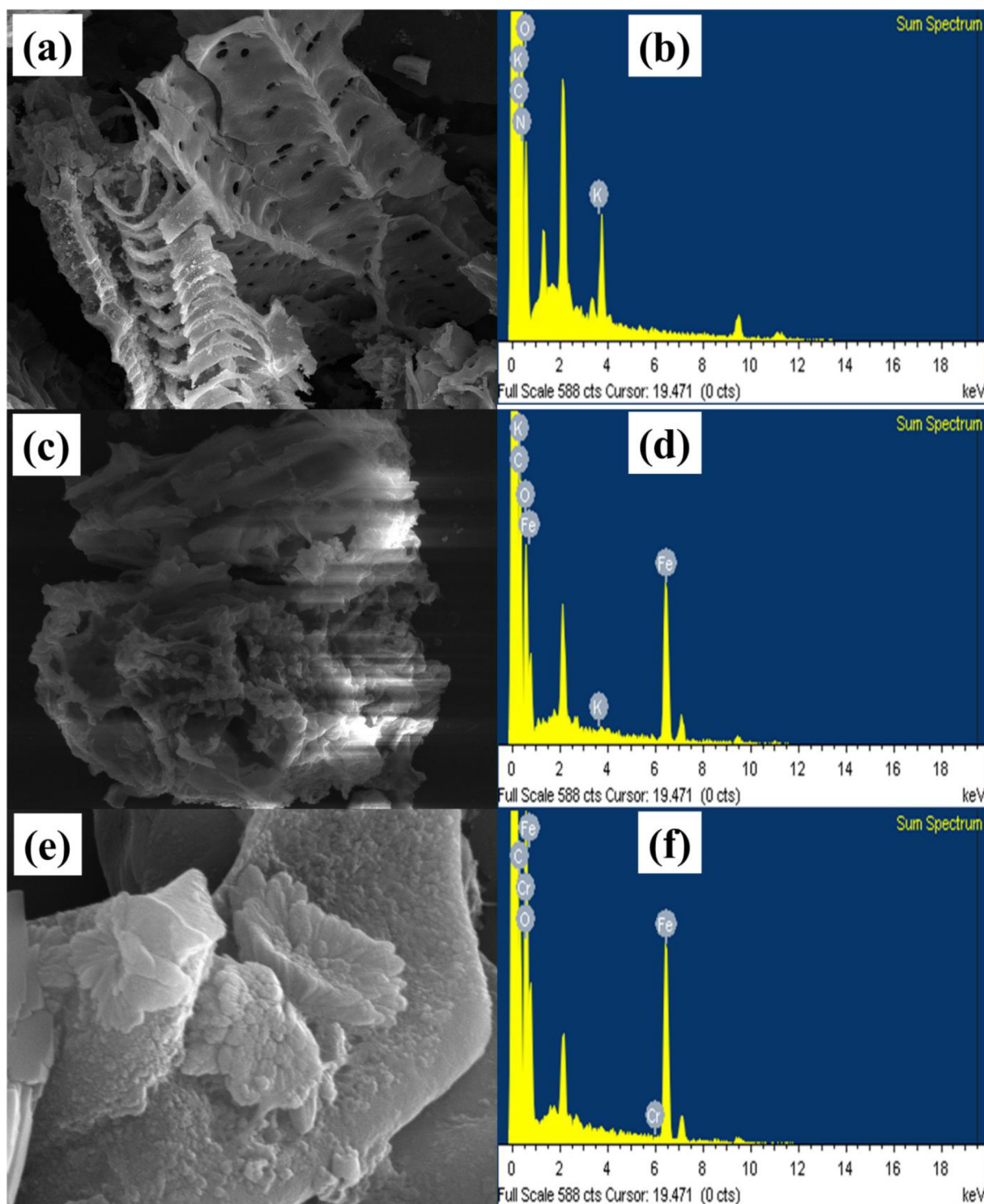


Fig. 1. FESEM and EDS images of MFSAC (a, b) and Fe₃O₄/MFSAC nanocomposite before (c, d) and after adsorption (e, f).

The FTIR analysis of the Fe₃O₄/MFSAC nanocomposite and MFSAC is displayed in Fig. 2. from Fig. 2a, it was noted that MFSAC possesses peak for -OH stretching vibration of several groups at 3383 cm⁻¹ [37]. The activated carbon's C-C vibration

was shown by the peaks at 1422 cm⁻¹. Aromatic rings and acids were discovered to have C=O and C=C peaks at 1720 cm⁻¹ and 1627 cm⁻¹, respectively [38]. Benzene and its derivatives' C-H bending vibrations were represented by the other two peaks, which

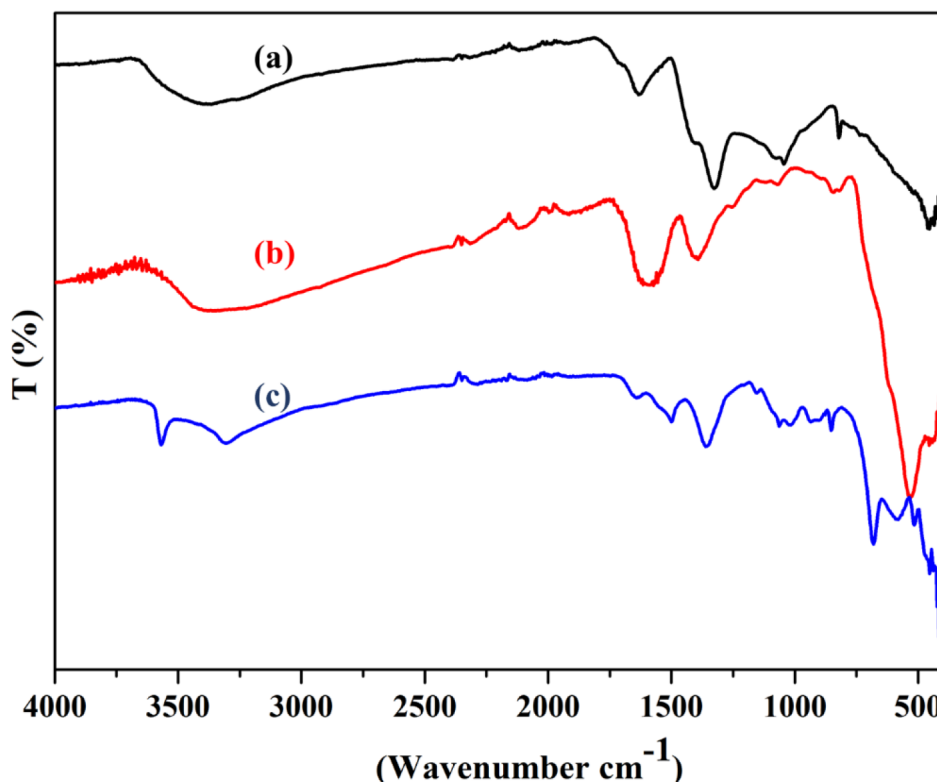


Fig. 2. FTIR spectra of (a) MFSAC and $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite before (b) and (c) after Cr(VI) adsorption.

were located at 1029 cm^{-1} and 450 cm^{-1} [39]. After Fe_3O_4 nanoparticles are decorated on the MFSAC surface, the FTIR bends have been repositioned, some lost completely, or newer ones have been created. This indicated the interaction between functional groups of MFSAC and Fe_3O_4 nanoparticles. Furthermore, a new peak that represented the Fe-O bond formed at 525 cm^{-1} [40]. The $\text{Fe}_3\text{O}_4/\text{MFSAC}$ FTIR spectrum following Cr(VI) adsorption is displayed in Fig. 2c. The peaks intensities were further decreased and -OH vibration bends at 3337 cm^{-1} were shifted to 3318 cm^{-1} . A new peak was appeared at 935 cm^{-1} for Cr-O vibrations, the $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite was thought to have absorbed Cr(VI) [41].

The XRD structure of MFSAC and $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite are shown in Fig. 3. The MFSAC shows a sharp peak at 26.49° for graphitic carbon [42]. The impurity phases of the activated carbon boehmit were represented by the peaks at 15.28° , 17.93° , and 21.19° . The benzene rings' carbon has an additional peak at 42.44° [43]. However, the activated carbon peaks vanished upon modification with Fe_3O_4 nanoparticles, and new peaks formed at angles of 30.07° , 35.37° , 43.15° , 53.59° , 57.17° , and 62.62° , which are subsequently attributed to crystal planes (220), (311), (400), (422), (511), and (440) [30]. These indicated the presence of a cubic spinal lattice of Fe_3O_4 nanoparticles. The removal

Table 1. Details BET analysis of $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite.

Sample	BET surface area (m^2/g)	Average pore size (nm)	Pore volume (cm^3/g)
$\text{Fe}_3\text{O}_4/\text{MFSAC}$	156.46	3.56	0.039

of activated carbon peaks was mostly caused by the surface development of Fe_3O_4 nanoparticles. This modification revealed the successful fabrication of the magnetic nanocomposite.

In Fig. 4, the isotherm curves for $\text{Fe}_3\text{O}_4/\text{MFSAC}$'s nitrogen adsorption and desorption are displayed. The nanocomposite displayed a type IV isotherm, as can be shown, confirming that micro and meso pores are present among the many pore sizes. The materials' mesoporous structure provides additional binding sites for Cr(VI) adsorption. The BET analysis data is detailed in Table 1. $\text{Fe}_3\text{O}_4/\text{MFSAC}$ was discovered to have a surface area of $156.46\text{ m}^2/\text{g}$, a pore diameter of 3.56 nm , and a pore volume of $0.039\text{ cm}^3/\text{g}$. As a result of the increased surface area, there are plenty of binding sites for the adsorption of Cr(VI) .

The zeta potential curve for the $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite is seen in Fig. 5. The nanocomposite has a significantly positively charged surface at lower pH 3, with a measured isoelectric point (pHIEP) of 5.91. The positively charged $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite surface would attract negatively

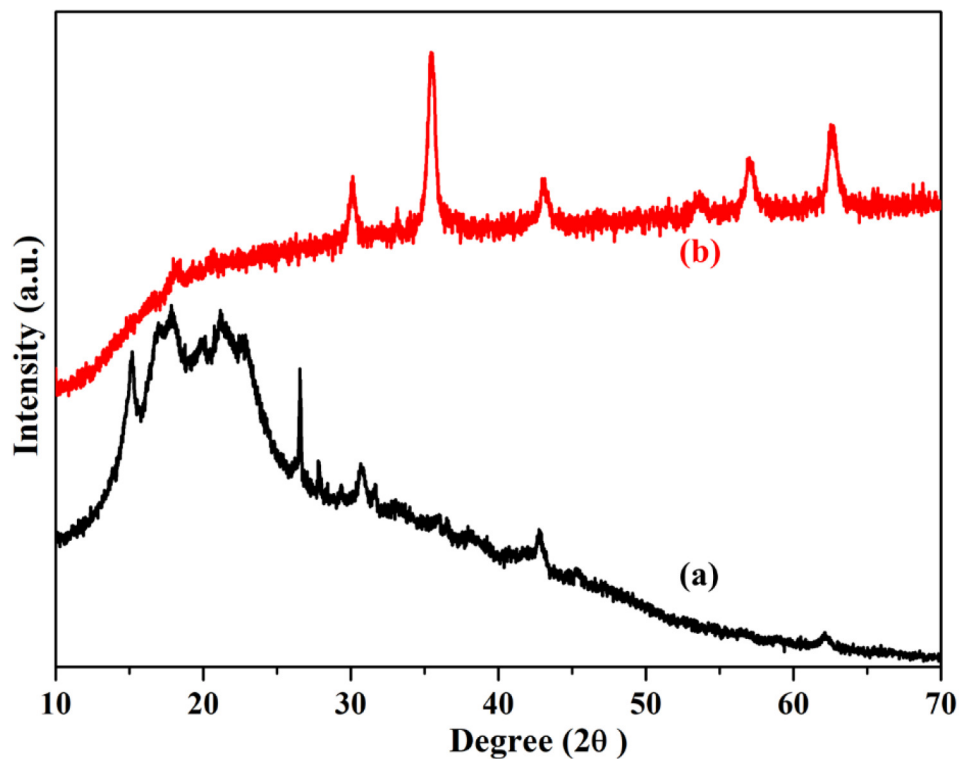


Fig. 3. XRD patterns of (a) MFSAC and (b) Fe₃O₄/MFSAC nanocomposite.

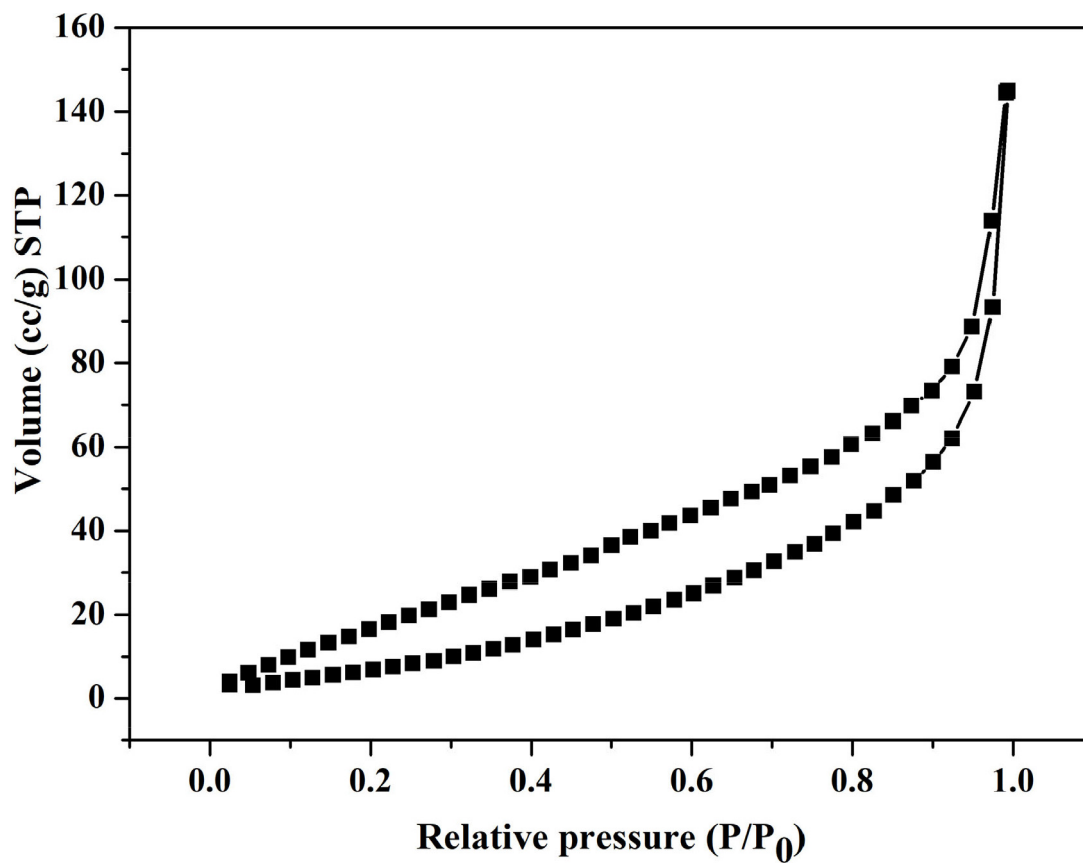


Fig. 4. BET isotherms curves of Fe₃O₄/MFSAC nanocomposite.

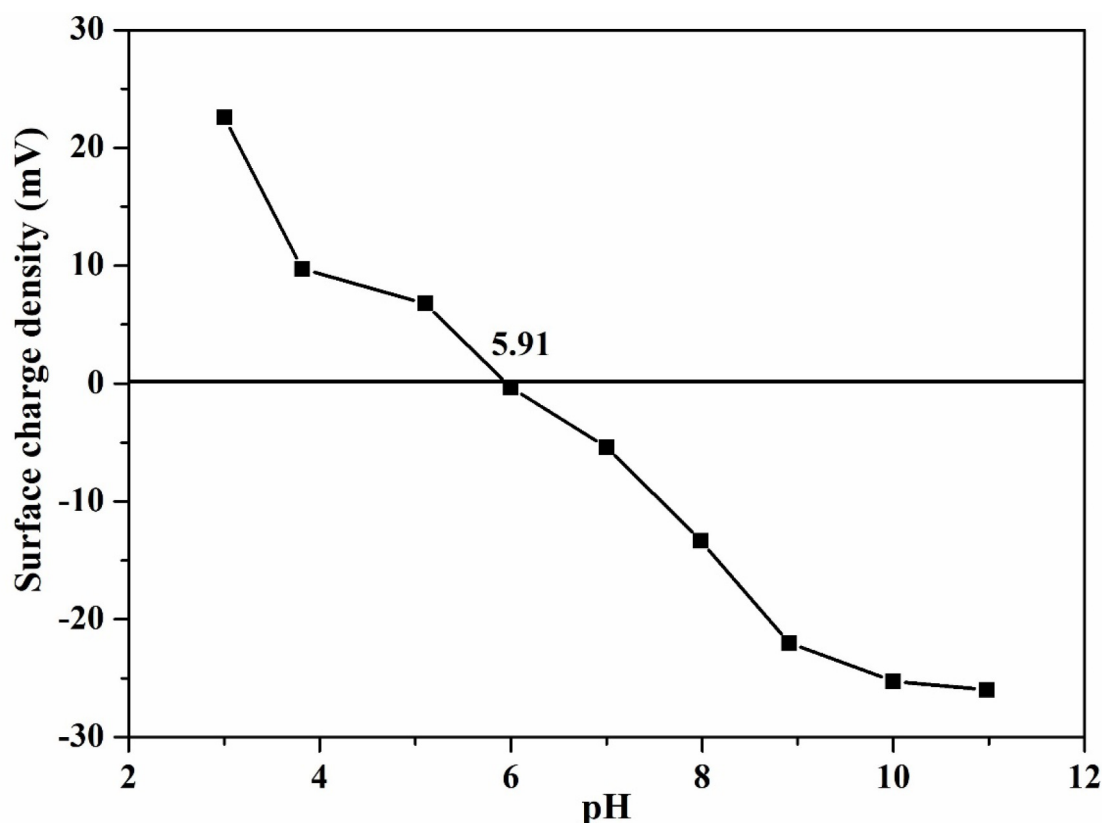


Fig. 5. pH_{IEP} of the Fe_3O_4 /MFSAC nanocomposite.

charged Cr(VI) ions exist as $HCrO_4^-$ ions (oxidation number +6) at the pH range of 2 to 6 in the aquatic environment) and be successfully extracted from the aqueous solution.

3.2. Application for Cr(VI) removal

3.2.1. Effect of adsorbent dose

The weight of the Fe_3O_4 /MFSAC nanocomposite was increased from 0.5 to 3 g in order to quantitatively eliminate Cr(VI). Fig. 6a displays the results of the elimination of Cr(VI) that was achieved. The Fe_3O_4 /MFSAC nanocomposite's absorption of Cr(VI) ions increased from 45% to 99% at dosages of 0.5 to 2.0 g before stabilising. After administering 2.0 g of adsorbent, the linearity indicated that equilibrium had been reached and that no more adsorption had occurred. This indicates that the removal of Cr(VI) was stabilised and that Cr(VI) ions had saturated the active sites on the Fe_3O_4 /MFSAC nanocomposite. It was discovered that 2 g was the ideal adsorbent dosage for the removal of Cr(VI) ions.

3.2.2. Effect of initial concentration

In this batch research, the adsorbent dose stays constant at 2 g, whereas the Cr(VI) ion concentrations

vary from 10 to 80 mg/L. According to Fig. 6b, the elimination increased from 80 to 93% as the concentration changed between 10 and 20 mg/L, and then, when the concentration rose, it sharply dropped. The existence of active spots on the surface of the Fe_3O_4 /MFSAC nanocomposite explains these findings. There were sufficient adsorption sites for Cr(VI) ions at lower starting concentrations (<20 mg/L), but as concentrations increased, the available adsorption sites became scarce and saturated, resulting in a decreased elimination efficiency. Several researchers utilising different kinds of adsorbents reported same findings [44]. Therefore, 20 mg/L was the ideal starting Cr(VI) concentration.

3.2.3. Effect of contact time

In the actual real-time application, time is a critical component. With an initial concentration of 20 mg/L and a constant adsorbent dosage of 2 g, the rate of removal of Cr(VI) as a function of contact time from 5 to 60 minutes is shown in Fig. 6c. Nearly 91% of the Cr(VI) was extracted from the mixture during the first 30 min of the contact time with the Fe_3O_4 /MFSAC nanocomposite, according to the results shown in the figure. The

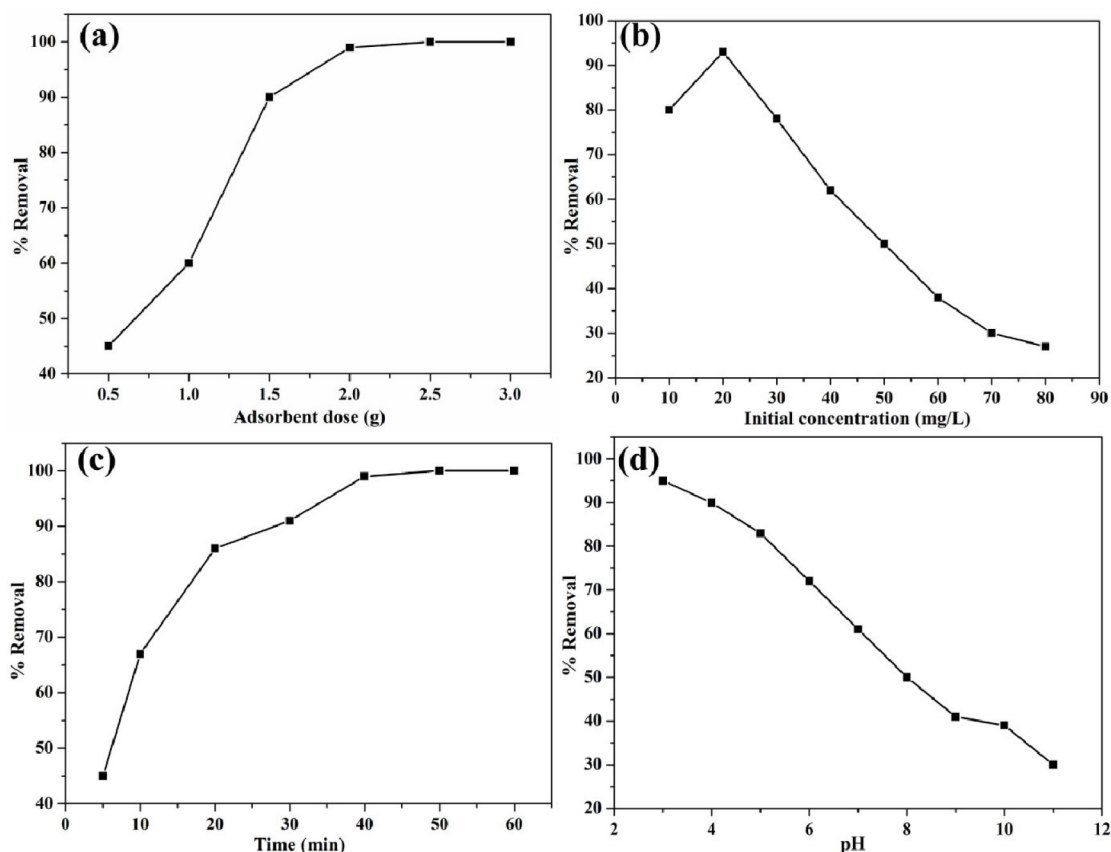


Fig. 6. Cr(VI) removal efficiency as a function of (a) adsorbent dose, (b) initial concentration, (c) contact time and (d) pH.

elimination rate rose to 99% after 40 min and was constant for the following 60 minutes. Because of the large number of active sites in the $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite, Cr(VI) ions may be easily accessible, resulting in fast Cr(VI) adsorption at lower times. Initially found on the $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite's surface, adsorbed Cr(VI) ions eventually dispersed throughout the pores and achieved equilibrium. Thus, 40 min is the optimal contact time for this investigation.

3.2.4. Effect of pH

Using a fixed adsorbent quantity of 2 g, an initial concentration of 20 mg/L, and a 40-min incubation period at room temperature, pH tests were conducted between 3 and 11 to eliminate Cr(VI). The most Cr(VI) was removed at pH 3, and the rate of removal of Cr(VI) decreased significantly at pH 6 (Fig. 6d). Below this pH level, the $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite's surface exhibits a positive charge; its pIIEP was 5.91 (Fig. 5). In the pH range of 2 to 6, HCrO_4^- is the most common type of Cr(VI) ions [45]. The positively charged $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite surface and the negatively charged

HCrO_4^- ions were therefore electrostatically drawn to one another. However, at higher pH values (neutral and alkaline conditions), Cr(VI) ions take the forms of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ [46]. These negatively charged Cr(VI) species therefore underwent electrostatic repulsion with the negatively charged $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite surfaces. Same time under alkaline conditions, excessive OH^- ions also compete with CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ about the adsorbent surface's adsorption sites, further decreasing the Cr(VI) removal [47].

3.3. Adsorption kinetics

Kinetics studies analyze the adsorption rate during the process of adsorption. It gives complete information about the time-dependent adsorption mechanism. In this swork, pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetics models were used to match the Cr(VI) removal data. Physical adsorption is explained by first-order kinetics, whereas chemical adsorption between the adsorbent and the adsorbate is explained by second-order kinetics. The following equations reflect

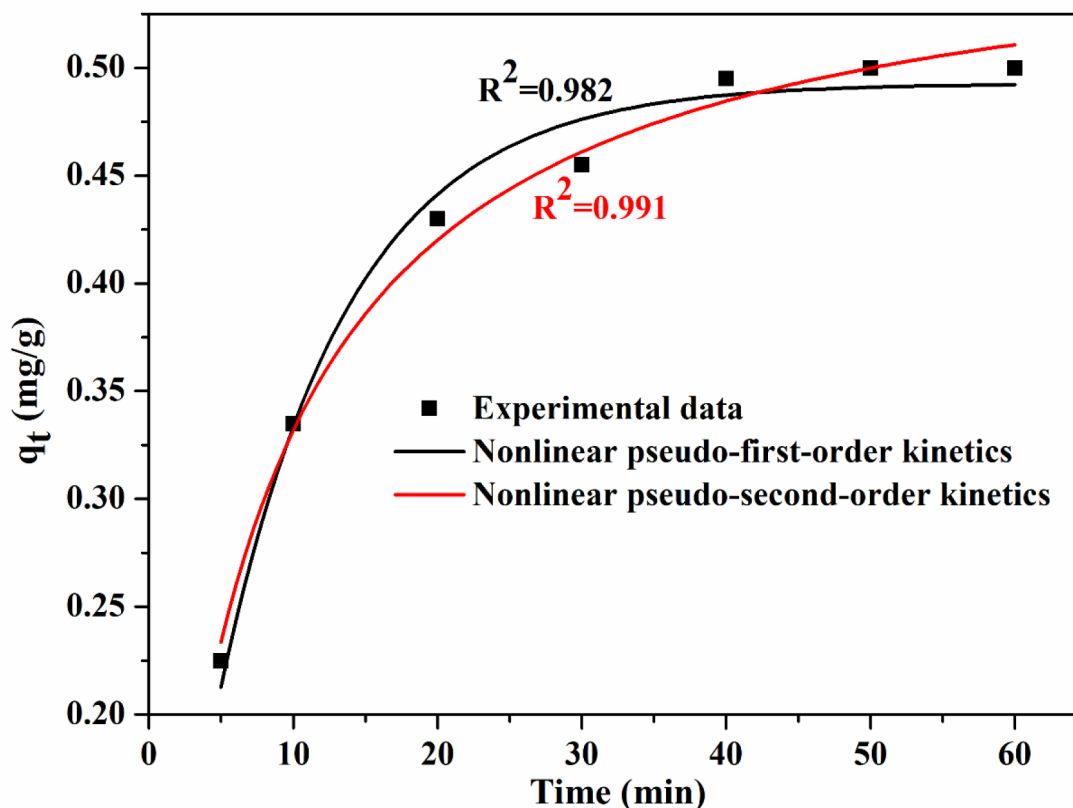


Fig. 7. Nonlinear kinetics for Cr(VI) removal.

the PFO and PSO nonlinear kinetics equations [48, 49];

$$q_t = q_e \left(1 - e^{-k_1 t}\right) \quad (3)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (4)$$

Adsorption capacity at equilibrium time is denoted by q_e , and adsorption capacity at time t is denoted by q_t . k_1 (min^{-1}) and k_2 (g/mg min) are rate constants of PFO and PSO, respectively. The PSO kinetics were suitably adjusted to the Cr(VI) removal, as seen in Fig. 7. Table 2 displays the parameters for the PFO and PSO kinetics models, respectively. The PSO's computed R^2 of 0.99 is much higher than the PFO kinetic model's R^2 of 0.98. This result demonstrated that there was chemical adsorption between the $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite and Cr(VI) ions [50, 51].

3.4. Adsorption isotherm

Isotherm studies examine how the adsorbate's molecules change the adsorbent's surface. Adsorption

Table 2. Pseudo-first-order and pseudo-second-order kinetic models' parameters.

Pseudo-first-order			Pseudo-second-order		
q_t (mg/g)	k_1 (min^{-1})	R^2	q_t (mg/g)	k_2 (g/mg min)	R^2
0.492	0.113	0.982	0.572	0.240	0.991

isotherm investigations have a direct bearing on the adsorption mechanism. This work has used Langmuir and Freundlich's isotherms to estimate the surface interaction between Cr(VI) ions and the $\text{Fe}_3\text{O}_4/\text{MFSAC}$ composite. The isotherms of Langmuir provide give information on homogenous adsorption whereas Freundlich isotherms signify the heterogeneity in the process of adsorption. In Eqs. (5) and (6) [52, 53], the nonlinear Freundlich and Langmuir isotherm equations are shown as follows;

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (5)$$

$$q_e = K_F C_e^{1/n} \quad (6)$$

The variables in this case are: C_e = Cr(VI) equilibrium concentration; n = heterogeneity factor;

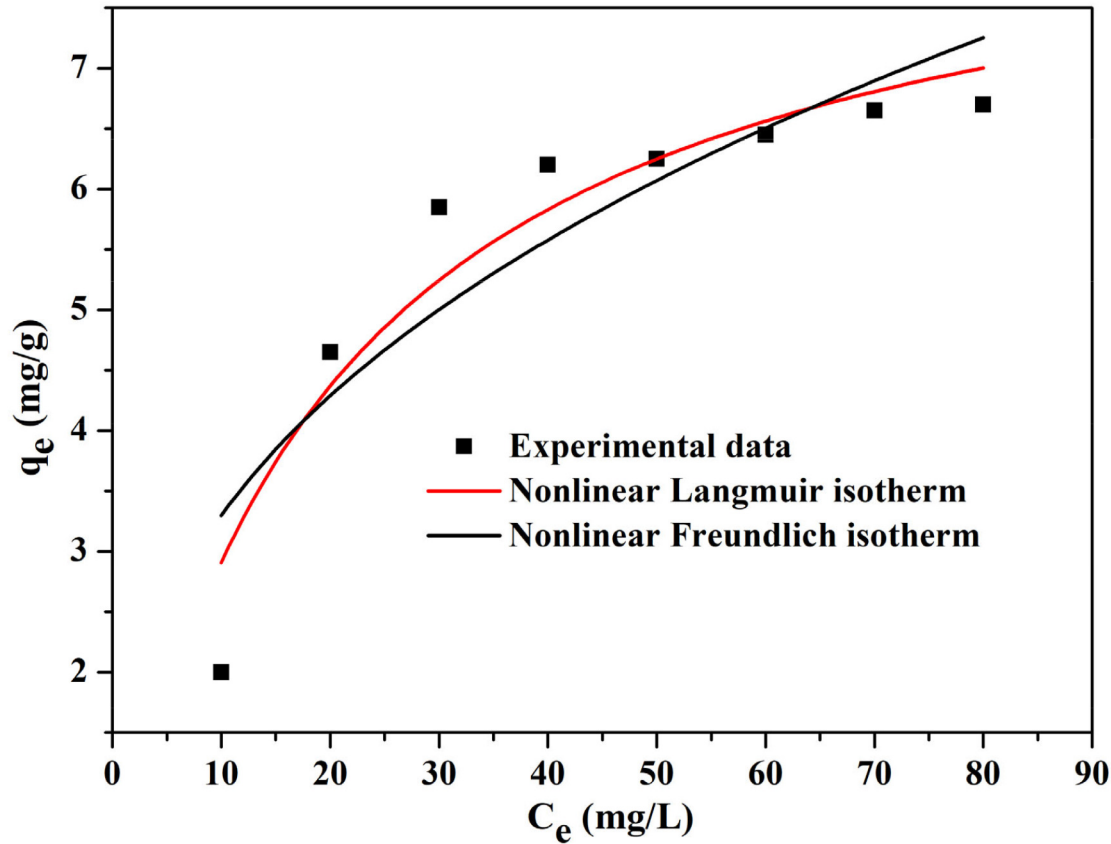


Fig. 8. Nonlinear isotherms for Cr(VI) removal.

Table 3. Nonlinear Langmuir and Freundlich isotherms parameter.

Langmuir isotherm		Freundlich isotherm	
q_m (mg/g)	8.76	K_f (mg/g)	1.37
b (L/mg)	0.04	n	2.63
R^2	0.89	R^2	0.78

Table 4. Cr(VI) adsorption capacities of different materials.

Adsorbents	q_m (mg/g)	References
γ -ALOOH/ α -Fe ₂ O ₃	1.79	[54]
Orange peel	7.14	[55]
Fe ₃ O ₄ -AC	8.06	[56]
Pineapple-peel-derived biochar	7.44	[57]
Fe ₃ O ₄ /MFSAC	8.76	Present study

K_F = Freundlich constant; q_e = equilibrium uptake capacity; b = Langmuir constant; and q_m = maximum uptake capacity. In Fig. 8, the nonlinear fitting curves for the Langmuir and Freundlich isotherms are shown. The Langmuir isotherms clearly made the best fit to the experimental data when compared to the Freundlich isotherm model. As shown in Table 3, the coefficient of correlation (R^2) for the Freundlich model is 0.78 and for the Langmuir model it is 0.89. The Fe₃O₄/MFSAC composite surface's Cr(VI) monolayer adsorption molecules were strongly demonstrated by this result [1]. The highest amount of adsorption capacity of Fe₃O₄/MFSAC composite is 8.76 mg/g. Comparison studies have been done with other materials and presented in Table 4.

3.5. Adsorption mechanism

This work's adsorption mechanism was described using FTIR and zeta potential measurements as basic techniques. From Fig. 2, the FTIR peak of OH groups of Fe₃O₄/MFSAC nanocomposite after adsorption had been removed and new peak also appeared at 935 cm⁻¹ for Cr-O vibration. This gave evidence that -OH groups were playing a drastic role in Cr(VI) adsorption. Again, the pH_{IEP} of Fe₃O₄/MFSAC nanocomposite was found to be 5.91. The positively charged Fe₃O₄/MFSAC nanocomposite surface (below pH 5.91) and the negatively charged Cr(VI) species were therefore interacting electrostatically. Hence, Cr(VI) was adsorbed on the Fe₃O₄/MFSAC

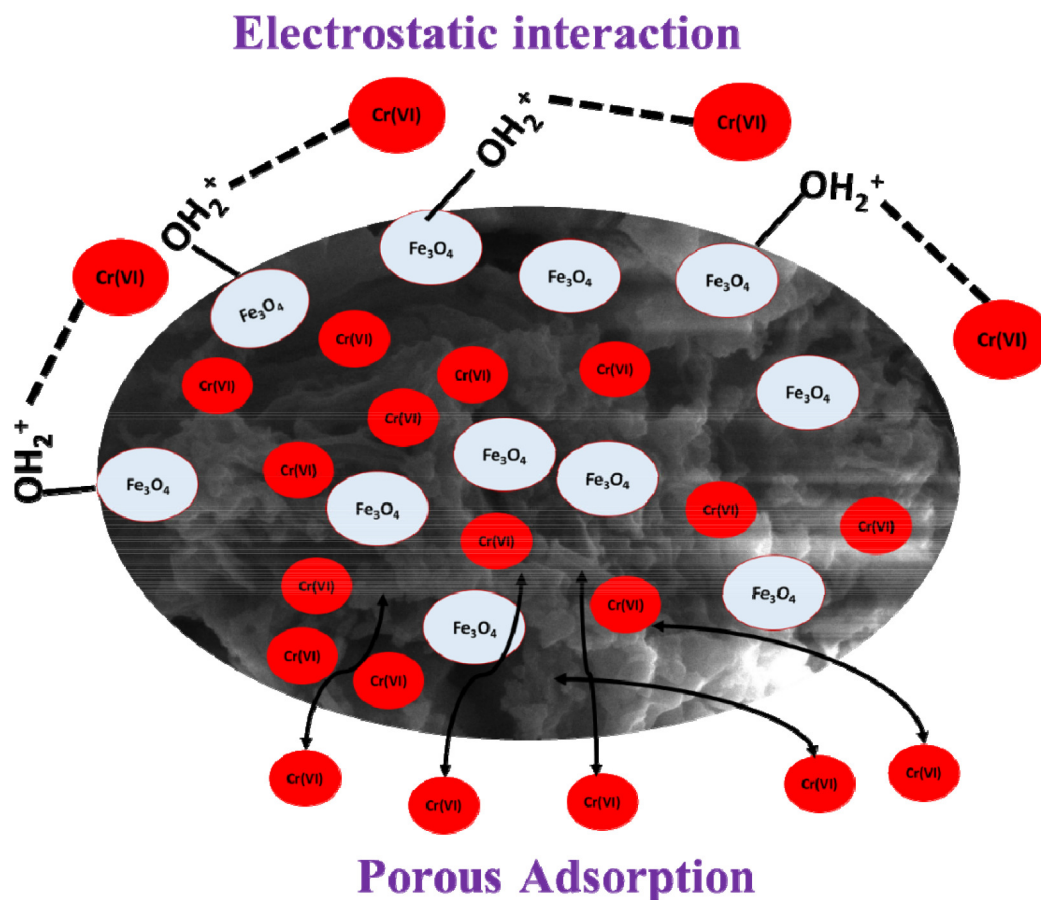


Fig. 9. Schematic representation of Cr(VI) removal mechanism on $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite surface.

nanocomposite surface by porous adsorption and electrostatic force of attraction. The suggested mechanism of this work is presented in Fig. 9.

4. Conclusions

A successfully prepared activated carbon from the waste marigold flower straw and Fe_3O_4 nanoparticles were decorated on its surface. The $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite production was verified by the use of XRD, FTIR, and FESEM instruments. The surface area of the nanocomposite is $156.46 \text{ m}^2/\text{g}$. In the optimal circumstances of adsorbent dose 2 g, starting concentration 20 mg/L, time 40 minutes, and pH 3, 99% of Cr(VI) was removed utilising the $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite. According to the isotherm analysis, the experimental results fit the Langmuir isotherm model, with an R^2 value of 0.89. Adsorption kinetics showed that chemical adsorption was possible using a pseudo-second-order model. Electrostatic attraction and porous adsorption were used to adsorb Cr(VI) ions onto the $\text{Fe}_3\text{O}_4/\text{MFSAC}$ nanocomposite surface. Overall, the results showed that using activated

carbon coated with magnetic iron oxide nanoparticles derived from waste marigold flower straw is a potential technique for extracting from aqueous solution of Cr(VI). This substitute adsorbent removes chromium ions from aqueous solutions in a way that is economical, highly effective, and ecologically benign.

Acknowledgments

The authors are also highly thankful to GIET University for providing the instrumental facilities to carry out the research work.

Conflict of interest

Authors declare no conflict of interest.

Ethical approval

Not applicable.

Data availability

Data will be provided on reasonable request.

Funding

This research received no external funding.

Author contribution

Shanmukha Rao Metta: Investigation, Formal analysis, Data curation and Writing original draft, Uttam Kumar Sahu: Supervision, Writing, review & editing original draft.

References

- Sahu UK, Zhang Y, Huang W, et al. Nanoceria-loaded tea waste as bio-sorbent for Cr(VI) removal. *Mater Chem Phys*. 2022;290:126563.
- Chen L, Zhang J, Zhu Y, Zhang Y. Interaction of chromium(III) or chromium(VI) with catalase and its effect on the structure and function of catalase: an in vitro study. *Food Chem*. 2018;244:378–385.
- Dhal B, Thatoi HN, Das NN, Pandey BD. Chemical and microbial remediation of hexavalent chromium from contaminated soil and mining/metallurgical solid waste: a review. *J Hazard Mater*. 2013;250–251:272–291.
- Ikegami K, Hirose Y, Sakashita H, et al. Role of polyphenol in sugarcane molasses as a nutrient for hexavalent chromium bioremediation using bacteria. *Chemosphere*. 2020;250:126267.
- Hamdan SS, El-Naas MH. Characterization of the removal of Chromium(VI) from groundwater by electrocoagulation. *Journal of Industrial and Engineering Chemistry*. 2014;20:2775–2781.
- Lin L, Xu X, Papelis C, et al. Sorption of metals and metalloids from reverse osmosis concentrate on drinking water treatment solids. *Sep Purif Technol*. 2014;134:37–45.
- Cao W, Wang Z, Ao H, Yuan B. Removal of Cr(VI) by corn stalk based anion exchanger: the extent and rate of Cr(VI) reduction as side reaction. *Colloids Surf A Physicochem Eng Asp*. 2018;539:424–432.
- Xia Q, Huang B, Yuan X, et al. Modified stannous sulfide nanoparticles with metal-organic framework: toward efficient and enhanced photocatalytic reduction of chromium (VI) under visible light. *J Colloid Interface Sci*. 2018;530:481–492.
- Abbasi-Garravand E, Mulligan CN. Using micellar enhanced ultrafiltration and reduction techniques for removal of Cr(VI) and Cr(III) from water. *Sep Purif Technol*. 2014;132:505–512.
- Xia Q, Huang B, Yuan X, et al. Modified stannous sulfide nanoparticles with metal-organic framework: toward efficient and enhanced photocatalytic reduction of chromium (VI) under visible light. *J Colloid Interface Sci*. 2018;530:481–492.
- Ma S, Song CS, Chen Y, et al. Hematite enhances the removal of Cr(VI) by *Bacillus subtilis* BSn5 from aquatic environment. *Chemosphere*. 2018;208:579–585.
- Onac C, Kaya A, Ataman D, et al. The removal of Cr(VI) through polymeric supported liquid membrane by using calix[4]arene as a carrier. *Chin J Chem Eng*. 2019;27:85–91.
- Li M, Chen X, He J, et al. Porous NiCo-LDH microspheres obtained by freeze-drying for efficient dye and Cr(VI) adsorption. *J Alloys Compd*. 2024;976:173107.
- Chen B, Zhao X, Liu Y, et al. Highly stable and covalently functionalized magnetic nanoparticles by polyethyleneimine for Cr(VI) adsorption from aqueous solution. 2015;5:1398–1405.
- Simeonidis K, Kaprara E, Samaras T, et al. Optimizing magnetic nanoparticles for drinking water technology: the case of Cr(VI). *Science of the Total Environment*. 2015;535:61–68.
- Ordóñez D, Valencia A, Chang N Bin, Wanielista MP. Synergistic effects of aluminum/iron oxides and clay minerals on nutrient removal and recovery in water filtration media. *J Clean Prod*. 2020;275:122728.
- Sahu UK, Mahapatra SS, Patel RK. Synthesis and characterization of an eco-friendly composite of jute fiber and Fe₂O₃ nanoparticles and its application as an adsorbent for removal of As(V) from water. *J Mol Liq*. 2017;237:313–321.
- López-García M, Martínez-Cabanas M, Vilarinho T, et al. New polymeric/inorganic hybrid sorbents based on red mud and nanosized magnetite for large scale applications in As(V) removal. *Chemical Engineering Journal*. 2017;311:117–125.
- Chen D, Li W, Wu Y, et al. Preparation and characterization of chitosan/montmorillonite magnetic microspheres and its application for the removal of Cr (VI). *Chemical Engineering Journal*. 2013;221:8–15.
- Singh V, Kumari P, Pandey S, Narayan T. Removal of chromium (VI) using poly(methylacrylate) functionalized guar gum. *Bioresour Technol*. 2009;100:1977–1982.
- Bée A, Talbot D, Abramson S, Dupuis V. Magnetic alginate beads for Pb(II) ions removal from wastewater. *J Colloid Interface Sci*. 2011;362:486–492.
- Ma MG, Zhu JF, Li SM, et al. Nanocomposites of cellulose/iron oxide: influence of synthesis conditions on their morphological behavior and thermal stability. *Materials Science and Engineering C*. 2012;32:1511–1517.
- Turner DJ, Pilling JE, Donahue M, et al. DAXA: traversing the X-ray desert by democratising archival X-ray *Astronomy*. 2024;2410:11954.
- Singh V, Kumari P, Pandey S, Narayan T. Removal of chromium (VI) using poly(methylacrylate) functionalized guar gum. *Bioresour Technol*. 2009;100:1977–1982.
- Babel S, Kurniawan TA. Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere*. 2004;54:951–967.
- Selvi K, Pattabhi S, Kadirvelu K. Removal of Cr(VI) from aqueous solution by adsorption onto activated carbon. *Bioresour Technol*. 2001;80:87–89.
- Hashem A, Abdel-Halim ES, El-Tahlawy KF, Hebeish A. Enhancement of the adsorption of Co(II) and Ni(II) ions onto peanut hulls through esterification using citric acid. *Adsorption Sci Technol*. 2005;23:367–380.
- Bai L, Liu Y. Kinetics of graft copolymerization of poly(hexanedioic acid ethylene glycol) and methyl acrylate initiated by potassium diperiodatocuprate(III). *J Appl Polym Sci*. 2007;103:2376–2381.
- Osifo PO, Webster A, van der Merwe H, et al. The influence of the degree of cross-linking on the adsorption properties of chitosan beads. *Bioresour Technol*. 2008;99:7377–7382.
- Sahu UK, Sahu S, Mahapatra SS, Patel RK. Cigarette soot activated carbon modified with Fe₃O₄ nanoparticles as an effective adsorbent for As(III) and As(V): material preparation, characterization and adsorption mechanism study. *J Mol Liq*. 2017;243:395–405.

31. Areti HA, Jabesa A, Daba BJ, Jibril D. Response surface method based parametric optimization of Cr(VI) removal from tannery wastewater using a mixed banana peel and corn cob activated carbon: kinetic and isotherm modeling studies. *Journal of Water Process Engineering*. 2024;59:104977.
32. Ozay O, Ekici S, Baran Y, et al. Removal of toxic metal ions with magnetic hydrogels. *Water Res*. 2009;43:4403–4411.
33. Badruddoza AZM, Shawon ZBZ, Tay WJD, et al. Fe₃O₄/cyclodextrin polymer nanocomposites for selective heavy metals removal from industrial wastewater. *Carbohydr Polym*. 2013;91:322–332.
34. Sahu UK, Sahu MK, Mahapatra SS, Patel RK. Removal of As(III) from aqueous solution using Fe₃O₄ nanoparticles: process modeling and optimization using statistical design. *Water Air Soil Pollut*. 2017;228:1–15.
35. Tripathy M, Padhiari S, Hota G. L-Cysteine-functionalized mesoporous magnetite nanospheres: synthesis and adsorptive application toward arsenic remediation. *J Chem Eng Data*. 2020;65:3906–3919.
36. Sahoo SK, Tripathy M, Hota G. In-situ functionalization of GO sheets with ALOOH-FeOOH composite nanorods: an eco-friendly nano-adsorbent for removal of toxic arsenate ions from water. *J Environ Chem Eng*. 2019;7:103357.
37. Danish M, Pin Z, Ziyang L, et al. Preparation and characterization of banana trunk activated carbon using H₃PO₄ activation: a rotatable central composite design approach. *Mater Chem Phys*. 2022;282:125989.
38. Mabalane K, Thabede PM, Shooto ND. Activated carbon from paper waste as potential adsorbents for methylene blue and hexavalent chromium. *Applied Sciences (Switzerland)*. 2024;14:4585.
39. Gu C, Cai M, He P, et al. Development of a natural iron-based mineral/biochar composite for efficient simultaneous removal of Cr(VI) and methylene blue in the presence of oxalic acid. *J Environ Chem Eng*. 2024;12:113301.
40. Bharath G, Rambabu K, Banat F, et al. Enhanced electrochemical performances of peanut shell derived activated carbon and its Fe₃O₄ nanocomposites for capacitive deionization of Cr(VI) ions. *Science of the Total Environment*. 2019;691:713–726.
41. Weckhuysen BM, Wachs IE, Schoonheydt RA. Surface chemistry and spectroscopy of chromium in inorganic oxides. *Chem Rev*. 1996;96:3327–3349. <https://doi.org/10.1021/cr940044o>.
42. Bahador F, Foroutan R, Esmaeili H, Ramavandi B. Enhancement of the chromium removal behavior of Moringa oleifera activated carbon by chitosan and iron oxide nanoparticles from water. *Carbohydr Polym*. 2021;251:117085.
43. Sahu UK, Tripathy S, Gouda N, et al. Eco-friendly neem leaf-based activated carbon for methylene blue removal from aqueous solution: adsorption kinetics, isotherms, thermodynamics and mechanism studies. *Journal of the Iranian Chemical Society*. 2023;20:2057–2067.
44. Sharma P, Monisha B, Kumar PS, et al. Effective removal of toxic mixed azo dyes and Cr (VI) ions from wastewater using an integrated approach. *Desalination Water Treat*. 2024;320:100654.
45. Sahu UK, Ji W, Liang Y, et al. Mechanism enhanced active biochar support magnetic nano zero-valent iron for efficient removal of Cr(VI) from simulated polluted water. *J Environ Chem Eng*. 2022;10:107077.
46. Kaur J, Kaur M, Ubhi MK, et al. Composition optimization of activated carbon-iron oxide nanocomposite for effective removal of Cr(VI) ions. *Mater Chem Phys*. 2021;258:124002.
47. Tu B, Chen H, Xue S, et al. Ultrafast and efficient removal of aqueous Cr(VI) using iron oxide nanoparticles supported on Bermuda grass-based activated carbon. *J Mol Liq*. 2021;334:116026.
48. Lagergren S. Zur theorie der sogenannten adsorption gelöster Stoffe, *Kungliga Svenska Vetenskapsakademiens. Handlingar*. 1898;24:1–39.
49. Ho YS, McKay G. Sorption of dye from aqueous solution by peat. *Chemical Engineering Journal*. 1998;70:115–124.
50. Sangkarak S, Kittipongvises S, Kitkaew D, et al. Influence of the iron-oxide mass fractions of magnetic powdered activated carbon on its hexavalent chromium adsorption performance in water. *Chemosphere*. 2024;364:142997.
51. Fang Y, Yang L, Rao F, et al. Behaviors and mechanisms of adsorption of MB and Cr(VI) by geopolymer microspheres under single and binary systems. *Molecules*. 2024;29:1–16.
52. Langmuir I. The constitution and fundamental properties of solids and liquids. *Journal of American Chemical Society*. 1916;38:2221–2295.
53. Freundlich H. Über die adsorption in Lösungen (adsorption in solution). *Journal of physical chemistry*. 1906;57:384–470.
54. Mikhaylov VI, Maslennikova TP, Krivosheina P V. Characterization and sorption properties of g-ALOOH/a-Fe₂O₃ composite powders prepared via hydrothermal method. *Mater Chem Phys*. 2017;186:612–619.
55. Ben Khalifa E, Rzig B, Chakroun R, et al. Application of response surface methodology for chromium removal by adsorption on low-cost biosorbent. *Chemometrics and Intelligent Laboratory Systems*. 2019;189:18–26.
56. Jain M, Yadav M, Kohout T, et al. Development of iron oxide/activated carbon nanoparticle composite for the removal of Cr(VI), Cu(II) and Cd(II) ions from aqueous solution. *Water Resour Ind*. 2018;20:54–74.
57. Wang C, Gu L, Liu X, et al. Sorption behavior of Cr(VI) on pineapple-peel-derived biochar and the influence of coexisting pyrene. *Int Biodeterior Biodegradation*. 2016;111:78–84.