

Removal of Chromium (VI) Ions from Polluted Water using Kaolinite-supported Fe/Al oxide(hydroxide) Composite Nanoadsorbents

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Hexavalent chromium (Cr (VI)) contamination of surface and groundwater has become a major environmental concern owing to the diverse applications of Cr(VI) in several industries. In the current study kaolinite-supported and size-controlled Fe/Al oxide(oxyhydroxide) nanocomposites (Kaolinite@Fe/Al nanocomposites) were synthesized for efficient removal of Cr(VI) from aqueous solution. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) analysis of the nanocomposites revealed that the nanocomposites were uniformly dispersed, with an average particle size of ~ 25 nm. Batch adsorption studies were carried out to study the effect of (Kaolinite@Fe/Al nanocomposites) on the removal of chromium (VI) from 100 mg/L Cr(VI) contaminated water over a wide pH range (3–10) at various adsorbent dosages. The result demonstrated that the nanocomposites' adsorption efficiency increased with increasing adsorbent dosage. When the Kaolinite@Fe/Al nanocomposites dosage was increased from 1.0 to 3.0 g/L, the Cr(VI) removal percentage increased from 65.4 % to ~99.0 %. This is due to the greater surface area and availability of more adsorption sites at higher dosages of the adsorbent. There was a significant removal of Cr(VI) in the pH range 3–6 reaching up to 99.0% Cr(VI) removal, however, removal efficiency decreased drastically beyond pH 6. Chromium (VI) exists as CrO_4^{2-} , HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ oxyanionic species while the surface of the adsorbent becomes highly protonated, owing to the variable surface charge imparted by Al/Fe oxides/hydroxides favouring remarkable uptake of Cr(VI) in the anionic form. The experimental data fitted Langmuir adsorption model well with a maximum adsorption capacity of 70.71 mg/g. The results of the study demonstrate that Kaolinite@Fe/Al nanocomposites may have a promising potential for remediation of Cr(VI) contaminated wastewater and industrial effluents.

1. Introduction

Heavy metals are common pollutants of water and soil, predominantly generated due to anthropogenic activities, posing risk for the ecosystems, due to their ubiquity, toxicity at a trace level, bioaccumulation, and persistence in the environment. Chromium is among these heavy metals listed by the US Environmental Protection Agency (USEPA) as one of the priority pollutants (Ali et al., 2019). Chromium is widely applied in many industries such as metallurgy, metal plating, leather tanning, and wood treatment, and chromium pollution of groundwater is usually caused by uncontrolled disposal or illegal discharge of industrial wastes (Wang et al., 2019). Chromium exists in several oxidation states, but Trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) are the most common and stable states in the natural environment. Under reducing conditions, chromium exists as Cr(III), by forming $\text{Cr}(\text{OH})_3$ or $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$ in the range of pH 6–11 which is immobile, insoluble, and less toxic (Li et al., 2020). Under oxidizing conditions, chromium exists as hexavalent chromium (Cr(VI)), chromate (CrO_4^{2-}), hydrogen chromate (HCrO_4^-) or/and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) oxyanionic species. Cr (VI) is highly mobile and is considered the most toxic form of chromium, as it presents high oxidizing potential, high solubility, and mobility across the membranes in living organisms and in the environment (Unceta et al., 2010). Hexavalent Cr is mutagenic, carcinogenic, and teratogenic state of chromium, recognized as a Group A human carcinogen by the United States Environmental Protection Agency (US EPA) with toxicity of 100–1000 times higher than Cr(III)

(Wang et al., 2019). The World Health Organization (WHO) set maximum contaminant limits for surface water of 0.1 mg/L, and the permissible limit is 0.05 mg/L for potable water (Xu et al., 2019). However, currently the concentration of Cr(VI) in contaminated surface and ground waters is 30–200 mg/L (Hosseini et al., 2021). Thus there is an urgent need to reduce the concentration of Cr(VI) in effluents to meet the permissible discharge limit. Several physicochemical and biological methods have been applied to remediate Cr(VI) from industrial effluents, soil, and groundwater hexavalent including ion exchange, chemical precipitation, electro-deposition, photocatalysis reduction, reduction, and adsorption (Yuan et al., 2009). Among these methods adsorption is generally considered to be the most suitable and efficient technology for the remediation of Cr(VI)-contaminated water bodies owing to its cost-effectiveness, design simplicity, performance and environmental benignity (Wei et al., 2019).

Kaolinite is an abundant clay mineral with a large specific surface area, chemical and mechanical stability, layered structure, and high cation exchange capacity making it an excellent adsorbent material. However, Kaolinite bears a negative surface charge under normal pH, making it inefficient to adsorb the anionic Cr(VI) species (Li et al., 2020). In recent years several studies have reported high anionic species adsorption potential of the binary Al/Fe composite oxides and oxyhydroxides (Alvarez-Ayuso et al., 2007). However, the nanocomposites have a strong tendency to aggregate due to their nanoscale size and subsequent high surface energy, significantly reducing surface/volume ratio, surface catalytic activity, and dispersion stability in the solution and their adsorption capacity (Zhu and Xu, 2016). Kaolinite could be a good candidate for dispersing binary Al/Fe oxides (oxyhydroxide) nanocomposite through the provision of nucleation sites for nanocomposite formation and prevention of aggregation of the nanocomposites. Additionally, the combination of the Al/Fe oxides (oxyhydroxide) nanocomposite and kaolinite adsorbents will synergistically enhance the Cr(VI) adsorption potential of the composite material. Thus, in the current study Kaolinite-supported Fe/Al oxides (oxyhydroxide) composite nanoadsorbents are produced for efficient adsorption of Cr(VI) from contaminated water.

2. Materials and methods

2.1 Synthesis of Kaolinite@ Fe/Al oxide/hydroxide nanocomposites

Kaolinite supported Fe/Al oxides (oxyhydroxide) nanocomposites (identified as Kaolinite@ Fe/Al oxides (oxyhydroxide)) were prepared by chemical co-precipitation method as previously reported by Chai et al. (2013). Briefly, 5.0 g of FeCl₃·6H₂O and 5.0 g of AlCl₃·6H₂O were dissolved in 100 mL deionized water. In another container, 2.5 g of finely ground nanoscale Kaolinite powder was added and stirred in 50 mL deionized water. Subsequently, the two solutions were mixed, and 1M NaOH solution was added dropwise into the solution, till the pH of the solution reaches 11, under vigorous stirring at 80 °C for 1 h in a nitrogen atmosphere. Afterward, the suspension was left to age for 24 h and then the nanocomposites were collected by centrifugation (10,000 rpm for 10 min) washed with deionized water thrice, and dried at 60 °C for 24 h to obtain the as synthesized nanocomposites. Next, the nanocomposites were characterized and used for adsorption study.

2.2 Characterization of Kaolinite@ Fe/Al oxide/hydroxide nanocomposites

The surface morphology and size distribution of the nanocomposites were studied using a field emission scanning electron microscope (FESEM, Zeiss 540 X-beam). A transmission electron microscope (TEM, Joel 2100) was applied for the characterization of the size and morphology of the as-synthesized nanocomposites at 200 kV.

2.3. Batch adsorption experiments

A series of batch adsorption experiments were performed in 250 ml Erlenmeyer filled with 100 mL aqueous 100 mg/L chromium VI solution adsorbent 0.2 g adsorbent, pH 5, and the flasks were placed on a rotary shaker and shaken at 150 rpm for 10 h at 25 °C. Afterward, the samples were collected, centrifuged (10000 rpm) for 5 min, the residual Cr (VI) concentration in the supernatant was determined spectrophotometrically using sodium 1,5-diphenylcarbazide at 540 nm wavelength (Rani *et al.*, 2017). All assays were carried out in triplicate and only mean values are presented. Percentage adsorption and adsorption capacity was determined

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (3)$$

Where R represents percentage removal, c_o (mg/L), c_t (mg/L), c_e (mg/L) represent initial concentration, concentration at time t , and equilibrium Cr(VI) concentrations respectively. V (mL) and m (g) represent volume of adsorption liquid and mass of adsorbent respectively

The effect of pH on Cr (VI) removal was examined by varying the pH of the solution from 3 to 10 using 0.1 M of HCl and 1M NaOH solutions with initial concentration of 100 mg/L. In order to determine the effect of adsorbent dosage, the quantity of the adsorbent was varied from 1.0 g/L to 4.0 g/L at optimal pH determined and initial Cr (VI) concentration of 100 mg/L. Adsorption kinetics study was performed at an adsorbent dose of 3.0 g/L, pH 5 and initial Cr (VI) concentration of 100 mg/L over 600 min contact time. Adsorption isotherm of Cr(VI) adsorption was studied by varying the initial Cr(VI) concentration from 10 to 200 mg/L at 3.0 g/L, pH 5 and adsorption time of 600 min long enough to reach equilibrium

3. Results and discussion

3.1 Characterization of the prepared samples

The TEM image in Fig.1a displays nanoparticles of uniform size of predominantly spherical morphology. The nanocomposites are of an average size ~25 nm, well dispersed on the kaolinite surface taking the site as a nucleation site for particle formation and growth. SEM images displayed in Fig. 1b confirm the uniform size distribution and nanoscale size of the particles. TEM and SEM images display that the Al/Fe oxide nanoparticles are homogeneously formed on the surfaces and edges of Kaolinite without agglomeration (Fig. 1b). The high surface area to volume ratio of the nanoparticles dispersed on the kaolinite surfaces would play a significant role toward achieving efficient Cr(VI) adsorption potential and reactivity.

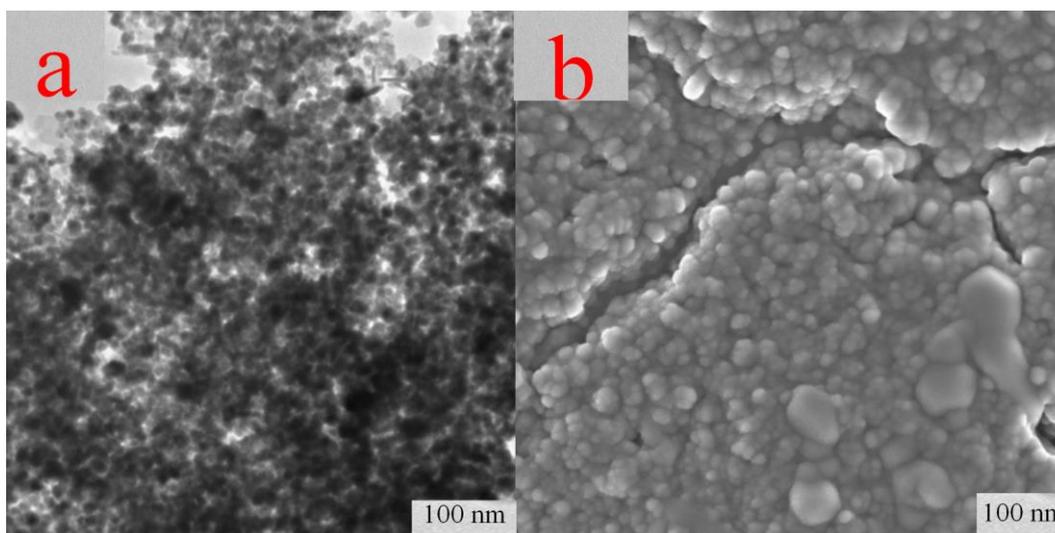


Figure 1: TEM images of the Kaolinite supported Fe/Al oxide/hydroxide nanocomposites (a); SEM images of Kaolinite @ Fe/Al oxide/hydroxide nanocomposite (b)

3.2. Adsorption study of Cr(VI)

In the adsorption study, the effect of adsorbent dose and pH of the solution on adsorption performance was studied. Solution pH is an important parameter as it determines the degree of ionization of the adsorbate and surface charge of the adsorbent (Lim et al., 2012). Figure 2a displays that the nanocomposite material retained high adsorption capacity toward Cr(VI) within a wide pH range (3.0–6.0). However, after pH 6 it showed drastic reduction in adsorption capacity of the adsorbent was observed. Chromium VI exists as anionic species CrO_4^{2-} , HCrO_4^- under normal oxidizing and pH range 2–7, and $\text{Cr}_2\text{O}_7^{2-}$ at higher pH values (Gładysz-Płaska et al., 2012). The higher adsorption at a wider pH range as opposed to the negative surface charge of clay kaolinite, may be attributed to the positive surface charge of the composite adsorbent imparted by the Al/Fe oxides and hydroxide nanocomposites (Jiang et al., 2012). However, as the pH increases beyond 6 the adsorption potential of the adsorbent decreased which may be attributed to the deprotonation of the adsorbent surface resulting in electrostatic repulsion between the anionic Cr(VI) species and hydroxyl saturated surface of the adsorbent.

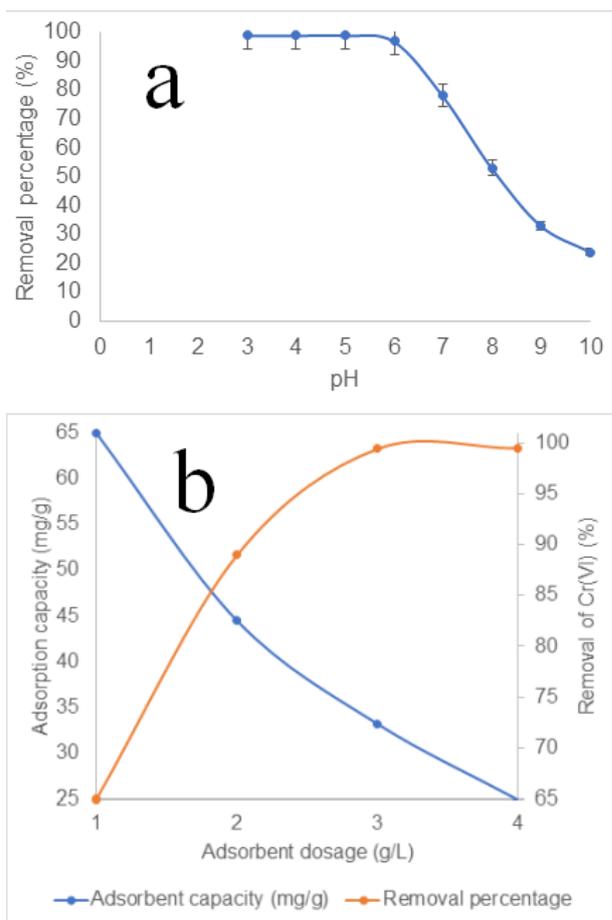


Figure 2: Effect of solution pH on Cr (VI) adsorption performance of Kaolinite@ Fe/Al oxide/hydroxide nanocomposite adsorbent (a); Effect of adsorbent dosage on equilibrium adsorption capacity and removal percentage of Cr(VI) (b)

Adsorbent dosage is an important factor that determines the amount of optimal dose required for a given initial concentration of Cr(VI). As demonstrated in Fig. 2b, the amount of Cr (VI) absorbed increased with an increase in adsorbent dosage. It can be observed that adsorption of Cr (VI) increased by 34.5 % as the adsorbent dosage increased from 1.0 g/L to 3.0 g/L. The increasing adsorption efficiency of the nanocomposite with increasing adsorbent dosage, can be attributed to the large number of vacant adsorption sites and the greater surface area favouring more Cr(VI) adsorption. Thus, the adsorbent dosage of 3 g/L was used as an optimal adsorbent dosage and applied in the subsequent adsorption studies. However, the adsorbent capacity of the adsorbent decreased as the adsorption percentage increased with increasing adsorbent dosage. The decreasing adsorption capacity with increasing adsorbent dosage maybe attributed to the increasing adsorbent mass, adding more adsorption sites, while the amount of adsorbate remains constant.

3.2 Adsorption isotherms

Adsorption isotherms describe the relationship between adsorbate and adsorbent at equilibrium at constant temperature and are important parameters in the design of efficient adsorption system. Equilibrium adsorption data were modelled using Langmuir and Freundlich equilibrium adsorption models, as represented by equations 4 and 5 respectively.

$$q_e = \frac{q_{max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (4)$$

$$q_e = K_f \cdot C_e^{\frac{1}{n}} \quad (5)$$

Where C_e (mg/L) is equilibrium concentration, q_e (mg/g) and q_{max} (mg/g) represent equilibrium and maximum adsorption capacities, K_L (L/mg) is the Langmuir equilibrium constant, K_F (L/g) is the Freundlich equilibrium constant, $1/n$ is adsorption intensity.

As represented in Fig. 3 and Table 1. the experimental equilibrium adsorption data fitted the Langmuir adsorption model well ($r^2 = 0.98$) compared to the Freundlich model ($r^2 = 0.95$) with a maximum adsorption capacity of 70.71 mg/g, demonstrating that the Cr(VI) adsorption process was monolayer. Similar studies of Kaolinite-assisted Cr(VI) adsorption have been reported by Angerasa et al.(2021). In contrast to several kaolinite assisted Cr (VI) adsorption studies reported in previous studies, the current study exploits the variable surface charge property of the composite adsorbent bearing positive valences attributed to the Al/Fe component offering it efficient adsorption potential of anionic species (Alvarez-Ayuso et al., 2007; Jiang et al., 2012).

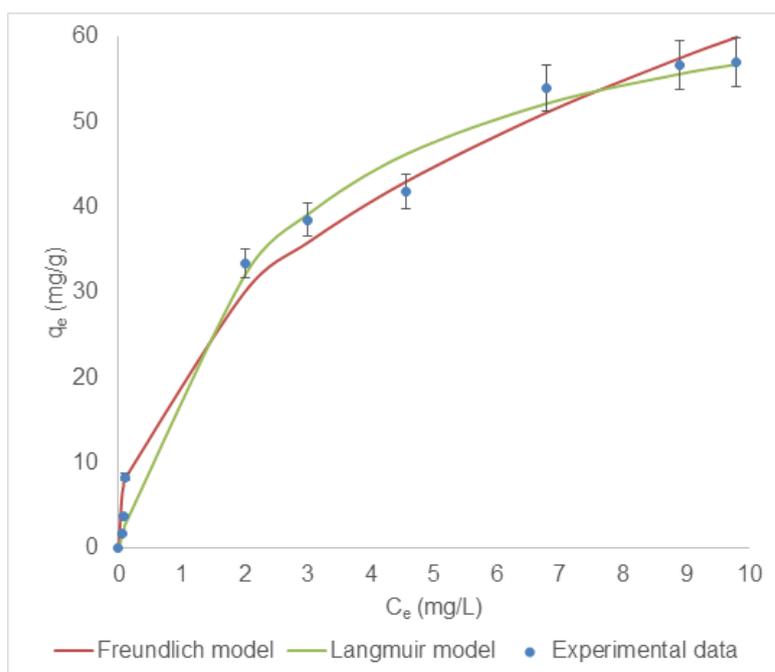


Figure 3: Freundlich and Langmuir equilibrium adsorption isotherm model fits of the experimental data.

Table 1: Best fit parameters of Freundlich and Langmuir equilibrium adsorption models with their associated correlation coefficients

Model	Parameters	Values \pm SD
Langmuir	q_{max}	70.71 ± 1.1
	K_L	0.41 ± 0.01
	r^2	0.98 ± 0.1
Freundlich	K_F	22.31 ± 1.1
	n	2.31 ± 0.2
	r^2	0.95 ± 0.1

4. Conclusions

In the current study, Kaolinite supported Fe/Al oxide(hydroxide) composite variable charge nano adsorbents were produced for efficient adsorption of chromium VI from contaminated water. The adsorbents demonstrated efficient Cr(VI) removal over the pH range (3–6). The equilibrium adsorption data fitted the Langmuir isotherm model well, demonstrating monolayered adsorption of Cr(VI). Besides serving as support for the Al/Fe oxide/oxydioxide composite nanoadsorbents the positive variable surface charge property of the composite increased the positive surface charge of the kaolinite clay synergistically improving the adsorption efficiency of the Kaolinite supported Fe/Al oxide(hydroxide) composite nano adsorbents.

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