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RESEARCH ARTICLE

Biopolymer-based fly ash-activated zeolite for the removal of chromium from acid mine drainage

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Abstract

Acid mine drainage (AMD), acid rock drainage, and fly ash from coal burning in power plants both posses widespread environmental and economic problems for many countries. Various biopolymers like chitosan have been used as a low-cost adsorbent for removal of toxic metals from AMD. The present investigation involves the microwave synthesis of low-cost chitosan biopolymer-based fly ash zeolite (CS@FAZ) adsorbent for the removal of chromium (Cr) from the acidic environment. The compositional and surface morphological characterization were conducted using fourier transform infrared (FTIR), x-ray diffraction (XRD), and scanning electron microscope (SEM), energy dispersive x-ray spectroscopy (EDS) analysis. The synthesized adsorbents were used for the removal of Cr (VI) ion under different experimental conditions, including initial concentration (15 – 60 mg L^{-1}), contact time (0 – 180 minutes), dose (0.25 – 4 g L^{-1}), solution pH (2 – 6). The optimum removal was 67.48% at room temperature 27°C, pH 3, concentration 45 mg L^{-1} and 0.1 g L^{-1} dose of CS@FZ adsorbent. The field evaluation parameters such as ionic strength and regeneration capacity show the adsorbent's potential applicability in the remediation of AMD. The kinetics models and adsorption isotherm were determined to be pseudo-second order ($R^2 > 0.8952$) validated with 27.78 mg g^{-1} maximum adsorption capacity and fitted by Freundlich isotherm ($R^2 > 0.9264$). The present low-cost adsorbent can be used for large scale to eliminate the Cr (VI) from the acid mine drainage.

Keywords: Fly ash activated zeolite, Chitosan biopolymer, Cr (VI) removal, Adsorption isotherm, Kinetics rate models.

Introduction

Acid mine drainage (AMD), is a major environmental concern, predominantly caused by the weathering of pyrite (FeS_2). Pyrite oxidizes to produce very acidic waters, which can solubilize heavy metals and other toxic elements and cause them to be transported downstream into river bodies, eventually ending up in the sea. Heavy metals are contained with high concentration in the effluent of many industries such as mining, metal processing, landfill leachate, pulp and paper; and pesticides (Guo *et al.*, 2020). Chromium (Cr), a profoundly hazardous pollutant, is generated by various industrial activities such as mining, electroplating, tanning, etc. Chromium exhibits polyvalent properties and primarily exists in Cr(VI) and Cr(III) forms. Due to its significant toxicity, it has been designated as a top-priority contaminant by the U.S. Environmental Protection Agency (EPA) (Zhou *et al.*, 2016). Cr(VI) compounds are known to be highly toxic, carcinogenic and mutagenic, which exhibit a higher toxicity than Cr(III) (Duan *et al.*, 2017). Therefore, It is significant to develop a low-cost and reliable technique to eliminate Cr(VI) from AMD before being discharged into aquatic and terrestrial systems.

A variety of treatment technologies to remediate Cr(VI) contaminated wastewater, including chemical precipitation, membrane separation, oxidation/reduction, ion exchange, adsorption, ultrafiltration and reverse osmosis, have been proposed (Zhang *et al.*, 2018). Among them, adsorption process has evolved as the frontline for Cr(VI) disposal because of its high selectivity, economic efficiency and operation simplicity (Guo *et al.*, 2020). Due to the advent of technology, the possibility of developing new low-cost adsorbents comprising of high surface area and rich chemical activity arises, subsequently improving water remediation methods (Reis *et al.*, 2021).

Chitosan (CS) is a deacetylation of chitin product, the second most naturally abundant polymer. It can be extracted from crustaceans such as prawns, crabs, fungi, and insects

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(Xie *et al.*, 2013). CS, a biosorbent with abundant amino and hydroxyl groups, shows excellent adsorption capacity toward both the inorganic and organic contaminants owing to the electrostatic attraction, hydrogen bonding, ion exchange, or Van der Waals force. It is a powerful adsorbent and catalyst because it has high surface area and quantity of reactive groups. Various researchers have explored many chitosan-based adsorbents to remove Cr(VI) ions. Similarly, with an increasing demand for coal-based thermal power plants and industries, the major environmental concern is handling surplus and unused quantities of fly ash. Currently, researchers are working to investigate the possible uses of fly ash in specific and practical fields. One of the measure areas in this context is a synthesis of zeolites from the fly ash. Based on this concept, many researchers have made efforts to synthesize fly ash zeolites by employing hydrothermal treatment, fusion and molten salt methods. The present work involves the synthesis of novelCS@FAZ composite adsorbent from CS and fly ash zeolite (FAZ) to avail benefits of both adsorbents for proving high removal efficiency at low cost in removal to Cr(VI) ions from acidic environment. The present study involves the comprehensive characterization of CS@ FAZ using fourier transform infrared (FTIR), x-ray diffraction (XRD), and field emission gun-scanning electron microscope-energy dispersive x-ray spectrometry (FEG-SEM-EDS) and pH ZPC along with various parameters of adsorption of Cr(VI) like optimum dose, removal efficiency, equilibrium and kinetic for preparing adsorption isotherms. The field applicability of the adsorbent was evaluated using the ionic strength and, regeneration & reusability for cost-effectiveness.

Material and Methods

Activation of Fly Ash Activated Zeolite

Waste fly ash collected from the Akrimota Thermal Power Station, Nanichher, Lakhpat, Kachchh, India (23.769788°N 68.645427°E) was used as a raw fly ash (FAR). The collected FAR sample was washed with deionized water (DIW) to remove the water-soluble inorganic components present in the FAR sample. Afterward, the sample was dried in a hot air oven at 60ºC for 5 hours to eliminate any moisture content. The FAR was reacted with the 2 N NaOH solution under microwave irradiation at 350 w for the (2×2) minutes. The resultant mixture was added 2 N HCL to active further to remove mineral waste (Ren *et al.*, 2020; Setiabudi *et al.*, 2017). The activated FAZ was washed with DIW to obtain a neutral pH 7. The FAZ sample was dried as above mentioned for FAR and store in a plastic container till further use for characterization and application.

Facile Synthesis of CS based Fly Ash Activated Zeolite (CS@FAZ) Adsorbent

The chitosan solution was prepared using the 1.8 g of commercial grade chitosan in the 1% v/v glacial acetic acid (GAA) 80 mL solution (Priyadarshi *et al.*, 2022; Raval *et al.*, 2022). Simultaneously, 0.2 g of FAZ powder was added in to 20 mL of GAA solution. Both the solutions were stirred vigorously, under the ultrasonication bath till the bobble free clear solution appeared. The solution was mixed and given microwave irradiation at 350 W for the 2 minutes duration with 5 times reptation. The reaction mixture was allowed to reach the room temperature. The 1 N NaOH was used to prepared chitosan biopolymer-based fly ash-activated zeolite composite (CS@FAZ) hydrogel beads. The CS@FAZ was agitated in the solution for the 2 hours. Afterward, the CS@FAZ beads were separated, washed with DIW and dried in hot air oven at 60℃ for 8 hours (Khan *et al.*, 2007; Khanday *et al.*, 2017).

Characterization of Synthesized Adsorbent

The functional groups identification of the raw and synthesized material CS, FAR, CS@FAZ before as well as after Cr removal CS@FAZ-Cr was conducted by FTIR spectra (Perkin Elmer spectrum 400) within the range of 400–4000 cm^{-1}. The X-ray diffraction (XRD) spectra of these samples were recorded between specific 2θ values (i.e., 5° – 80°) by powder XRD Bruker D8 Advance to comprehend the crystal structure of the materials. The morphological and compositional characterization of CS@FAZ before and after Cr removal CS@FAZ-Cr was performed using SEM (JEOL JSM-7600F) and EDS analysis, respectively. The pH_{ZPC} of the synthesized adsorbent was estimated using the pH drifting method (Khan *et al.*, 2007; Khanday *et al.*, 2017).

Adsorption Experiment for Cr(VI) Removal

The 500 mg L^{-1} standard Cr(VI) stock solution was prepared by dissolving 141.4 mg $K_2Cr_2O_7$ in 100 mL of DIW. The working standards having various concentrations of Cr solution was achieved by diluting stock solution and confirmed with the standard curve ($R^2 = 0.981$). Cr(VI) was estimated using the UV-visible spectrophotometer based diphenylcabazide method. To establish the synthesized adsorbent CS@FAZ at the laboratory scale, the role of the system parameters (i.e., initial Cr(VI) concentration (15, 20, 25 30, 45 and 60 mg L^{-1}) with contact time at 30 minutes interval (0–180 minutes) and dose (12.5 – 200 mg) was identified by performing the batch studies. The selection of the low concentrations such as 15 to 60 mg L^{-1} and contact time was based on their frequent detection in AMD, as per the study conducted by (Dhal *et al.*, 2013). The removal% and maximum adsorption capacity (q_m) for the present study were evaluated using the following equations.

$$\mathrm{Cr(VI)\ removal\ \%} = \frac{(\mathrm{Initial\ Cr(VI)\ concentration}\ (C_0) - \mathrm{Final\ Cr(VI)\ concentration}\ (C_e))}{\mathrm{Initial\ Cr(VI)\ concentration}\ (C_0)} \times 100\ \%$$

$$\mathrm{Maximum\,Cr(VI)\ sorptioncapacity}\ (\mathrm{q_e}) = \frac{(C_0 - C_e) \times (volumeof\,\mathrm{Cr(VI)}solution\ (v))}{(\mathrm{dryweight(W)ofCS@FAZ})}$$

Where, C_0 and C_e are in mg/L, W is in gm and V is in L.

Adsorption kinetic experiments were performed with different Cr(VI) concentrations at pH 3 and room temperature. The obtained results were used to calculate the adsorption kinetic parameters using the pseudo-first order, pseudo-second order and intraparticle diffusion models. Langmuir, Freundlich and Temkin isotherm models were selected to examine the equilibrium results.

Identification of Potential Applicability of CS@FAZ Toward Simulated AMD

To identify the probable applicability of CS@FAZ towards the AMD treatment, the cost-benefit aspect (regeneration study), and implication due to presence of various acidic anions (*via* ionic strength study).

Studies of salt solution implications on Cr(VI) removal efficiency

The presence of various ions and pollutants in acid drainage from mines, the influence of different ions at varying concentrations on the removal efficiency of Cr(VI) using CS@FAZ was investigated. In a standard reaction procedure, 100 mg of the adsorbent CS@FAZ were submerged in 50 mL of a Cr(VI) solution containing 30 mg L^{-1} concentration at various pH depending upon pH of ionic solution. This solution contained individual acid solutions, including HCl, HNO_3, H_3PO_4, and H_2SO_4, each at 1 and 50 mM concentrations. The mixture was agitated for 60 minutes.

Desorption and reusability studies of CS@FAZ towards Cr(VI)

To identify the regeneration capacity of the synthesized adsorbent CS@FAZ, the immediate adsorption and desorption process was performed in a batch mode. Initially, 0.1 g of CS@FAZ was initially agitated with 50 mL of Cr(VI) solution with 30 mg/L concentration for 180 minutes. Afterwards, the Cr(VI) saturated beads were separated by filtration process, dried in an oven (55–65°C) for 12 hours. These dried beads were desorbed by agitating in 50 mL of NaOH solution (1N) for 60 Minutes at 55°C heating and stirring. Then after regenerated beads separated and dried for its second and subsequent adsorption-desorption cycles up to the five cycles. The recovered Cr(VI) using NaOH solution was measured using the same method as described in section 2.3.

Results and Discussion

Characterization of the CS, FAR, CS@FAZ and CS@ FAZ-Cr

FTIR

FTIR of CS and FAZ (a), CS@FAZ before & after Cr removal CS@FAZ-Cr (b). The IR spectrum of CS represents the absorption peaks at 3557, 3418, and 3239 cm^{-1}, corresponding to the stretching vibrations of-OH groups and $-NH_2$, respectively. Also, the asymmetric stretching vibrations (vs) of $-CH_3$ of the CS molecule were identified at 2927 cm^{-1} wavenumber. The peak and band detected at 1622 and 1386 cm^{-1} were ascribed to the bending and stretching vibration of the $-CONH_2$ (Amide) and amide III (C-N) groups, respectively. The broad peak and stretching vibrations were detected at

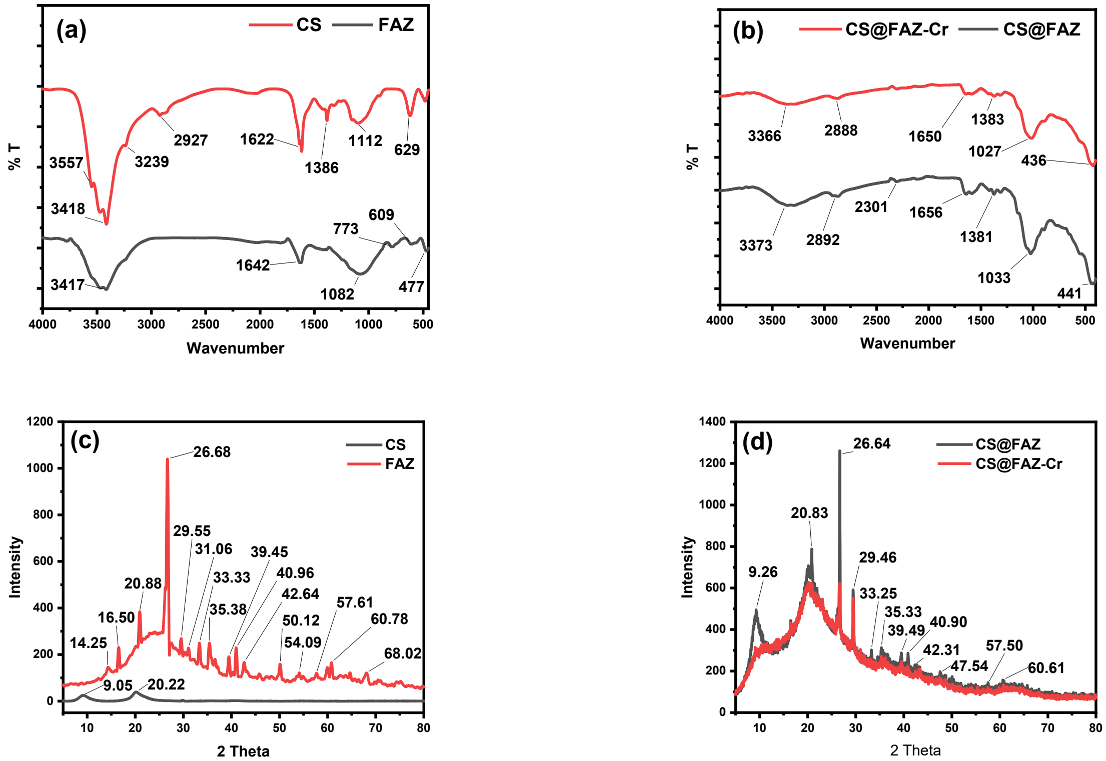

Figure 1: (a) FTIR of CS and FAZ, (b) CS@FAZ before & after Cr removal CS@FAZ-Cr and; (c) XRD spectra of CS and FAZ; and (d) CS@FAZ before & after Cr removal CS@FAZ-Cr.

1112 and 629 cm^{-1} wavenumbers, which show -CO (pyranose ring) and -C_2H_5NO (N-acetyl) groups (Wen *et al.*, 2011). The FTIR spectrum of the synthesized FAZ in Figure 1(a) shows the bands of fly ash at 1642, 1035, 773 and 477 cm^{-1} that represent the absorption peaks of asymmetric Si–O–Si bond stretching, symmetric Si–O–Si bond stretching and vibration of aluminum oxide, respectively (Yang *et al.*, 2019). Also, other stretching vibrations at 3417 and 609 cm^{-1} indicated the presence of –OH and Al–O (Kantiranis *et al.*, 2006) in the FAZ sample. Figure 1(b) shows the spectrum of CS@FAZ at 3373 and 2892, representing the -OH and -NH_2 group of chitosan biopolymer present on the surface (Wen *et al.*, 2011). The bands at 1033 and 441 cm^{-1} represent the asymmetric and symmetric stretching vibrations corresponding to zeolite's SiO4 or AlO4 structure (Khanday *et al.*, 2017). The adsorption peak of CS@FAZ-Cr at 3366 cm^{-1} shifted after Cr(VI) adsorption from 3373 $cm^{-1,}$ which indicates that the interaction between Cr metal ion and chitosan through –OH and –NH group (Hidayat *et al.*, 2023; Zhang *et al.*, 2021). Another peak at 1650 cm^{-1} was shifted from the 1656 cm^{-1} after the Cr(VI) adsorption that corresponds to the carboxylic group. Similarly, all the adsorption peaks were shifted and the %transmission have been increased in each the spectra of CS@FAZ-Cr.

XRD

Figures 1 (c and d) represent the XRD spectra from 5 to 80°2θ value of various samples CS and FAZ (c) and CS@ FAZ before and after Cr removal CS@FAZ-Cr (d). Figure 1(c) exhibits two distinct and prominent peaks of chitosan biopolymer at 2θ values of 9.83 and 20.05 serve as compelling evidence that the crystal structure, predominantly existing in a hydrated form, has been confirmed (Priyadarshi *et al.*, 2022). The XRD analysis of the FAR revealed the presence of distinct and sharp peaks corresponding to quartz at 2θ value 26.68° and calcite at 2θ value 29.55° (Setiabudi *et al.*, 2017). Figure 1 (d) represents the corresponding peak of CS@ FAZ for the CS and FAZ, both at 2θ values with slightly swift to 9.26, 20.83 and 26.64, respectively. After the adsorption of Cr(VI), the XRD spectra show no peak at 9.26° and a reduction in peak at 20.83, which shows that adsorption reduces the intramolecular crystallinity of CS (Zhang *et al.*, 2021). Similarly, the Quarts and mullite peak at 2θ values 26.64, 29.46, 33.25, 35.33 etc., show reduction after the adsorption of Cr (VI) in the CS@FAZ sample that confirmed the comparative amorphous surface to the CS@FAZ.

FEG-SEM-EDS

The size and shape of the synthesized CS@FAZ before & after Cr removal CS@FAZ-Cr was studied by analyzing the FEG-SEM images. The surface morphology and elemental composition of and CS@FAZ-Cr samples are depicted in Figure 1 (a and c) SEM images. The SEM image of CS@FAZ sample shows abundant pores on the surface, which favored transfer and adsorption of Cr (VI). Calcium and some other acid-soluble salts were dissolved, some coarse exterior and new cavities appeared during the acidification process (Li *et al.*, 2006). Similarly, the FAZ has found the formation of a polycrystalline aggregate of zeolite with crystallite size ranging up to 2–3 µm can be clearly observed in the morphology of CS@FAZ corresponds to previous studies (Kazemian *et al.*, 2010). After the Adsadsorption has been found that the cavities in the surface of the CS@FAZ (refer Figure 1 (a)) were filled by the large size granules (refer Figure 1 (c)) which is due to the adsorption of Cr(VI).

The EDS spectra and elemental composition (wt%) for CS@FAZ before and after Cr removal CS@FAZ-Crare are presented in Figures 2 (b and d) and Table 1. The CS@FAZ sample observed the various minerals such as K, Mg, Fe and Si etc. peaks, while after the Cr (VI) adsorption (CS@FAZ-Cr) samples, it has found this element by the dissolution of these elements at pH 4 or it may have been replaced with Cr (VI) through ion exchange process (Kutchko & Kim, 2006; Li *et al.*, 2006). It also found that 4% increase the Cr element in the sample CS@FAZ-Cr compared to the CS@FAZ which confirmed the adsorption process take place on the surface of CS@FAZ.

Cr(VI) Removal Experiment

The Cr(VI) removal efficiency of CS@FAZ was evaluated with various operating parameters and the obtained results are depicted in Figures 3 (a-f).

Effect of initial Cr(VI) concentration with contact time

The Cr(VI) removal for CS@FAZ adsorbent with regard to the initial concentration (15, 20, 25, 30, 45 and 60 mg L^{-1}) and agitation time (0, 15, 30, 60, 90, 120, 150 and 180 minutes) is provided in Figures 3 (a & b). At the initial 90 minutes, Cr (VI) concentration from 15 to 60 mg L^{-1}, with an average CR (VI) removal of 45.18% with adsorbent CS@FAZ. Furthermore, approximately 5% increment was found in the Cr(VI) removal till 150 minutes for the studied adsorbent. After that only 1% increment was found for the further 30 minutes, which shows the equilibrium archived at 180 minutes. The observation stated that increasing in Cr(VI) concentration adsorbed as it found more space to the CS@FAZ adsorbent up to the 45 mg L^{-1} (67.47% R). However, it shows a nominal decrease for 60 mg L^{-1}. This concentration gradient serves as a crucial driving force that facilitates the movement of Cr(VI) ions across the interface between the solid and liquid phases. This gradient effectively helps overcome any resistance encountered during the transfer process between the solid material and the surrounding liquid solution (Zheng *et al.*, 2020).

Effect of solution pH

The pH of the solution notably influences the adsorption process through two key mechanisms. The pH of the solution can induce changes in the surface charge of the adsorbent CS@FAZ. Under varying pH conditions, the surface of the adsorbent may acquire a positive or negative charge. This alteration in surface charge plays a pivotal role in the adsorption process because it affects the interaction between charged ions in the solution and the adsorbent CS@FAZ (Priyadarshi *et al.*, 2022). Apart from that, solution pH can also affect the solubility and ionization of Cr (VI)ions, which exists in anionic form such as $HCrO^{4-}$ and $Cr_2O_7^{2-}$ at pH 2 to 7 (Mohan & Pittman, 2006; Xu *et al.*, 2019). The pH of the solution can influence the degree to which Cr(VI) ions remain in a dissolved, ionized form or precipitate as solids. This, in turn, affects their availability for adsorption onto the adsorbent material. Figure 3 (c) shows the maximum adsorption took place at pH 3 with 51.49%. Further increase in the pH from (4 – 6) shows the gradual reduction in Cr(VI) removal (47.61 – 29.86%). The pH_{ZPC} of the adsorbent obtained at pH 6.9 indicates that it has a positive charge on the surface of the adsorbent below this pH. The protonated ions of CS@FAZ such as NH_3^+, OH_3^+ and Al_3^+ in acidic solution cause electrostatic attractions with anionic Cr(VI) species, leading to increased removal efficiency (Wen *et al.*, 2011). Reason for the reduction in %R, at pH 2 solution that chitosan molecule can dissolved from the adsorbent surface which led to increase in the concentration of Cr(VI) in the solution (Zhang *et al.*, 2021).

Effect of CS@FAZdose

The synthesized CS@FAZ in different amounts (12.5 – 200 mg) were added in 50 mL of 30 mg L^{-1}Cr (VI) concentration solution at pH of 3. Figure 3 (d) shows that CS@FAZ, the maximum Cr(VI) removal of 60.30% was achieved at 100 mg of adsorbent. The plausible explanation for this phenomenon is that, as the adsorbent dosage increases, the number of effective active sites and the available surface area for adsorption also increase (Yang *et al.*, 2016). The increase in dose from 100 to 200 mg of adsorbent only 12% Cr(VI) removal was increased because with increasing adsorbent doses, limited Cr(VI) ions have more adsorption space were available (Zhang *et al.*, 2021).

Identification of Potential Applicability of CS@FAZ Towards AMD

Studies of salt solution implications on Cr(VI) removal efficiency

Figure 3 (e) represents the performance of the CS@FAZ beads towards the removal of Cr(VI) in the presence of various ions mostly found in the acid drainage mine with toxic heavy metals. Therefore, different acidic solutions (HCl,

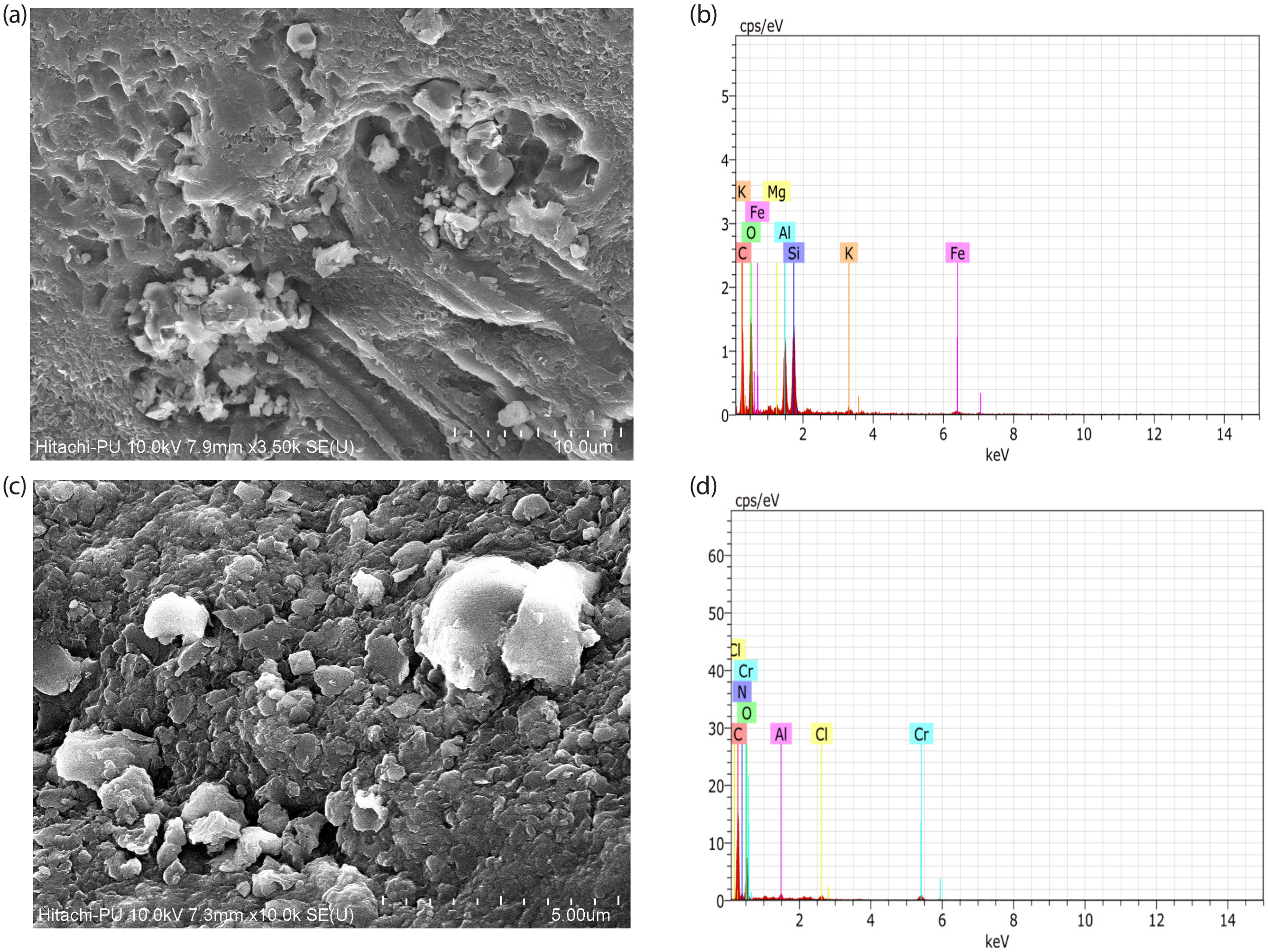

Figure 2: (a and b) SEM microphotographs and EDS spectra of CS@FAZ before & (c and d) after Cr removal CS@FAZ-Cr.

Table 1: Elemental composition of CS@FAZ and CS@FAZ-Cr using EDX analysis

Elememtal composition	*CS@FAZ(wt%)*	*CS@FAZ-Cr(wt%)*
Carbon	40.76	45.08
Oxygen	37.82	35.02
Silicon	10.15	0.1
Aluminium	7.43	0.27
Iron	2.56	--
Magnesium	0.58	--
Potassium	0.7	--
Chromium	0.0	4.56
Total	100%	100%

HNO_3, H_3PO_4, H_2SO_4) containing 1 and 50 mM ionic solution were used to evaluate the ionic strength towards Cr(VI) adsorption. The obtained results show that at higher (50 mM) ionic concentrations the Cr(VI) removal is decreased in H_2SO_4, HNO and HCl while increased in and H_3PO_4. A similar observation was found by (Zhang *et al.*, 2016).

Desorption and reusability studies of CS@FAZ towards Cr (VI)

The systematic desorption experiments were performed in an acidic condition to identify the regeneration ability of the synthesized adsorbents, essential for the multiple time application towards the contaminant removal. Figure 3 (f) shows that the Cr(VI) removal capacity was 45.8% decreased after the 5th cycle. The adsorption efficiency remained 83.94%

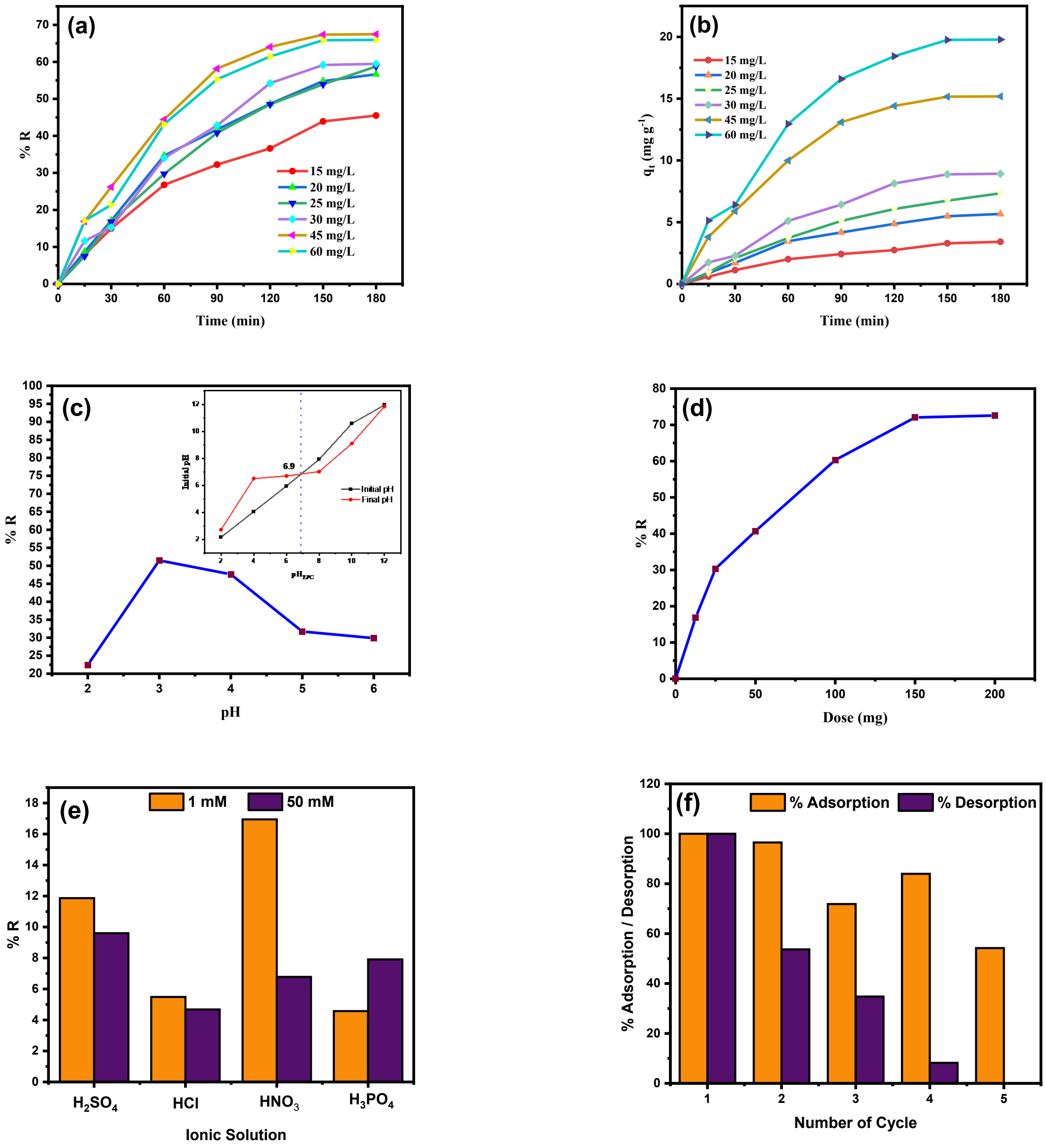

Figure 3: Optimization of the experimental parameters for the removal of Cr(VI) i.e., (a) different concentrations and contact time using CS@FAZ % removal and (b) q_e (mg g^{-1}), (c) effect of pH and (d) effect of adsorbent dose and (e) Ionic strength and (f) regeneration cycles study.

after the 4th regeneration cycle, showing better reusability of the adsorbent. Therefore, CS@FAZ could be easily reused for Cr(VI) adsorption with NaOH treatment upto the 4th cycle. However, lower desorption capacity (only 26.87%) after the second regeneration cycle suggests that it can't be applicable for recovering the Cr(VI) ion from the AMD.

Cr(VI) Adsorption Isotherms and Kinetics

The Cr(VI) adsorption data obtained from studies at equilibrium were plotted against the equilibrium adsorbate concentration in the liquid phase, as shown in Figures 4 (a-c). This analysis aimed to determine the suitability of three isotherm models, Langmuir, Freundlich and Temkin, in describing the experimental data. The calculated isotherm parameters and constants, along with their respective regression coefficient values (R^2), are presented in Table 2. For adsorbentCS@FAZ, consistently higher R^2 values were obtained for the Freundlich isotherm model, affirming its appropriateness for fitting the experimental data. This observation suggests that the adsorption of Cr(VI) ions onto the heterogeneous surface of CS@FAZ occurs through

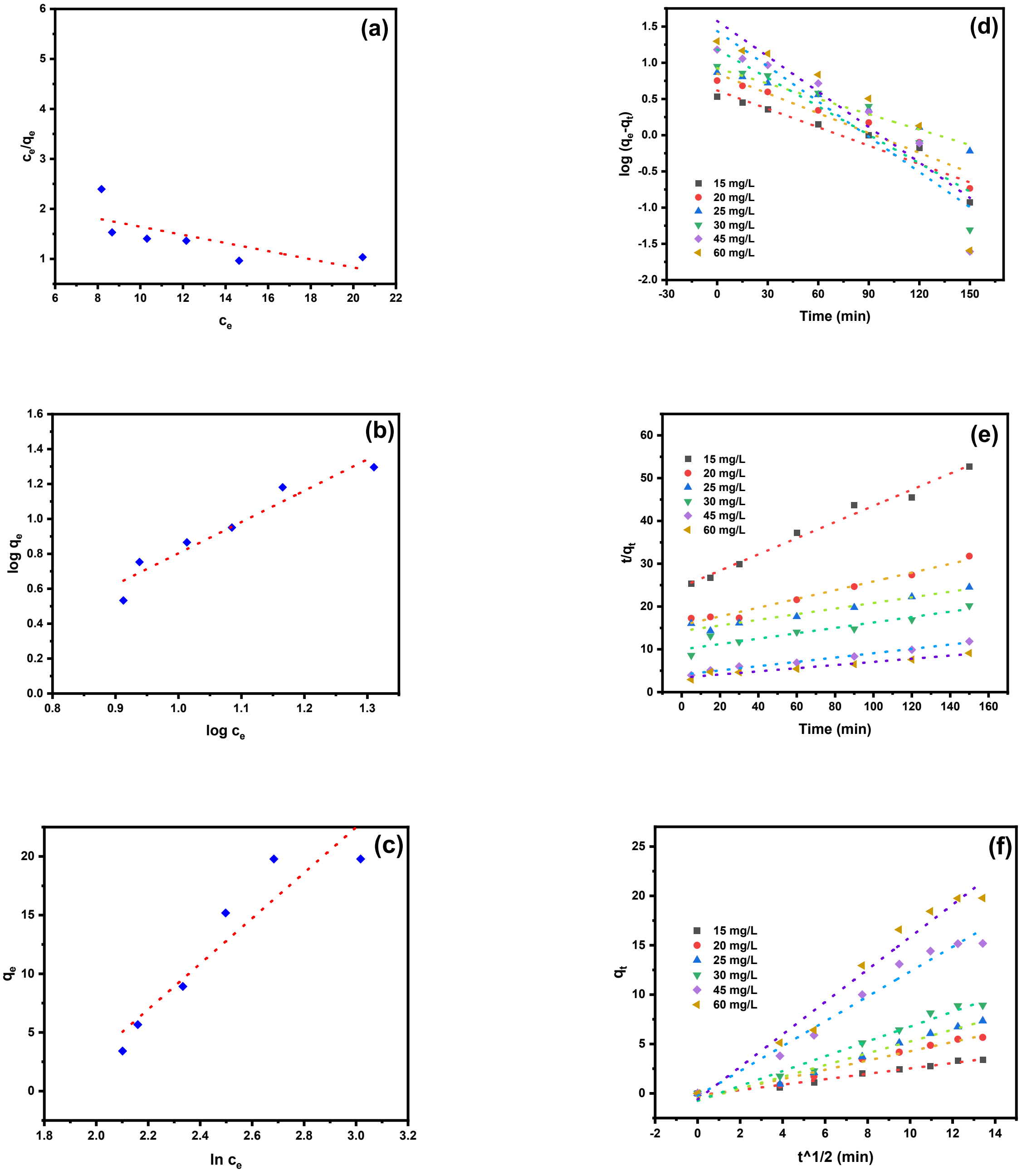

Figure 4: Isotherm modelling; (a) Langmuir, (b) Freundlich and (c) Temkin, (d) kinetic study pseudo-first-order, (e) pseudo-second-order a and (f) Intrapartile diffusion model (C_0 = 15 to 60 mg L^{-1}) for the removal of Cr(VI) onto the synthesized adsorbent CS@FAZ.

multilayer adsorption. The Langmuir adsorption capacity (q_m) was calculated to be 12.27 mg g^{-1}, indicating their significant ability to adsorb Cr(VI) ions. Furthermore, the values of the Freundlich constant (n) suggest that physical adsorption processes primarily govern the adsorption of Cr(VI) onto CS@FAZ. This finding further supports the suitability of the Freundlich isotherm model for describing the adsorption behavior.

Table 2: The Langmuir, Freundlich and Temkin isotherm parameters calculated for the adsorption of Cr (VI) on the surface of CS@FAZ.

Isotherm model	*Isotherm parameters*	*CS@FAZ*
Langmuir isotherm	qm(mg g^{-1})	12.27
	k_L(L g^{-1})	0.20
	R^2	0.5317
Freundlichisotherm	K_F(mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	0.1024
	n	0.5577
	1/n	1.7931
	R^2	0.9264
Temkin isotherm	KT (L/mg)	0.1588
	BT J /mol	19.381
	R^2	0.8808

Various kinetic rate models were applied to gain insights into the adsorption kinetics of Cr(VI) onto CS@FAZ, including the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. The results of these models are depicted in Figure 4 (d-f), and the corresponding parameters and rate constants are presented in Table 3, along with the regression coefficient values (R^2). The results indicate that both the studied rate models fit well with the experimental data, suggesting that the adsorption of Cr(VI) ions onto CS@FAZ is primarily driven by physically mediated chemisorption. Notably, in the case of CS@FAZ, the pseudo-second-order model exhibited a higher R^2 value, confirming that the adsorption of Cr(VI) is mainly mediated by chemisorption. The Weber-Morris intraparticle diffusion model was employed to elucidate the diffusion mechanism of Cr (VI) ions onto CS@FAZ. Figure 4 (f) shows that the results confirmed a rapid single-phase sorption process for CS@FAZ. However, the intraparticle diffusion model could not distinguish between the transport phase and equilibrium phase, suggesting that the adsorbents may have unoccupied sites available to accommodate the contaminant molecules. The calculated intraparticle diffusion constants are provided in Table 3.

Table 3: The pseudo-first-order, pseudo-second-order and intra-particular diffusion rate models calculated for the adsorption of on the surface of Cr (VI) on the surface of CS@FAZ

Kinetic models		*Rate parameters for the adsorption Cr (VI)*			
Pseudo-first-order constants	C_0 (mg L^{-1})	$q_{e(exp)}$ (mg g^{-1})	$q_{e(cal)}$ (mg g^{-1})	k_1 (min^{-1})	R^2
	15	3.4	0.0196	4.1467	0.8974
	20	5.7	0.0210	7.0811	0.9388
	25	7.3	0.0164	8.4217	0.9803
	30	8.9	-0.0302	15.2230	0.8388
	45	15.2	0.0374	27.3716	0.8612
	60	19.8	0.0375	37.7225	0.8192
Pseudo-second-order constants	C_0 (mg L^{-1})	$q_{e(exp)}$ (mg g^{-1})	$q_{e(cal)}$ (mg g^{-1})	k_2 (g $mg^{-1}min^{-1}$)	R^2
	15	3.4	5.39	0.0014	0.9851
	20	5.7	10.00	0.0006	0.9711
	25	7.3	15.63	0.0003	0.9439
	30	8.9	16.03	0.0004	0.8952
	45	15.2	20.24	0.0006	0.9899
	60	19.8	27.78	0.0004	0.9639
Intraparticular diffusion	C_0 (mg L^{-1})	$q_{e(exp)}$ (mg g^{-1})	K diff	C	R^2
	15	3.4	2.7420	-2.1706	0.9842
	20	5.7	4.6936	-4.2967	0.9750
	25	7.3	5.9719	-7.1771	0.9756
	30	8.9	7.5132	-7.4989	0.9685
	45	15.2	12.5800	-2.4881	0.9731
	60	19.8	16.4340	-6.0427	0.9708

Conclusion

The present investigation was focused on microwave-assisted low-cost acid-activated FAZ for the rapid synthesis of chitosan biopolymer-based fly ash zeolite (CS@FAZ) composite adsorbent has proven to be a promising approach for the efficient removal of Cr from acidic environments. The synthesized adsorbent's compositional and surface morphological properties were well-established through a comprehensive characterization using FTIR, XRD, and SEM-EDS analysis. The experimental investigation revealed that the CS@FAZ adsorbent exhibited good efficacy in removing Cr(VI) ions, with an optimum removal efficiency of 67.48% achieved under specific conditions, including a solution pH of 4, an initial concentration of 45 mg L^{-1}, and a dose of 0.1 g L^{-1} at room temperature. Furthermore, the study explored the adsorbent's potential applicability in the context of AMD, with promising results in terms of ionic strength and regeneration capacity. The adsorption kinetics were well-fitted by the pseudo-second-order model, indicating the strong affinity of the adsorbent for Cr(VI) ions, and the Freundlich isotherm model provided a good fit for the adsorption process. The maximum adsorption capacity was determined to be 27.78 mg g^{-1}. Overall, this low-cost CS@FAZ adsorbent demonstrates great potential for large-scale applications in the removal of Cr(VI) from acid mine drainage, addressing a critical environmental concern while offering a cost-effective and efficient solution. This research contributes significantly to the field of environmental remediation and provides a viable approach for tackling Cr(VI) contamination in acidic wastewater streams.

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