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Removal of hexavalent chromium ions using micellar modified adsorbent: isothermal and kinetic investigations

 Sadaf Sarfraz,^a Safdar Ameer,^a Mohsin Javed,^b Shahid Iqbal,^b  Samar O. Aljazzar,^d Manzar Zahra,^a Shahid Amin,^e Khizar Hussain Shah,^f Mohammed A. S. Abourehab,^{g,h} Eslam B. Elkaeed,ⁱ  Nasser S. Awwad^j and Hala A. Ibrahim^{k,l}

Hexavalent chromium is a very poisonous oxyanion and has had a negative impact on human health. This study assessed the viability of removing chromium(vi) using micellar modified adsorbents. In this study, chromium(vi) was removed from locally accessible wheat bran using separate applications of anionic sodium dodecyl sulfate (SDS) and cationic cetyltrimethylammonium bromide (CTAB) surfactants. The initial chromium content (5–12 ppm), pH (2–12), adsorbent dose (1–6 g/100 mL), agitation time (15–240 min), agitation speed (50–300 rpm), and temperature (15–50 °C) were all varied in the adsorption investigation. Pseudo first-order and second-order kinetic models were utilized to analyze the kinetic investigation. To determine thermodynamic parameters, the van't Hoff relationship was used. The maximum result for chromium(vi) uptake was obtained as 87.7%, 83.5% and 98.9% for WB, SDS-mWB, and CTAB-mWB, respectively, at an agitation time of 240 min (*i.e.*, 4 h), temperature (*i.e.*, 25–30 °C), agitation speed (150 rpm). However, both WB and CTAB-mWB derives metal ion removal at lower pH levels (2–4), whereas SDS-mWB requires a pH between 4 and 6 for maximum percentage removal of Cr(vi). The equilibrium data of WB and SDS-mWB were modeled by the Langmuir adsorption isotherm, while the data of CTAB-mWB fitted well in the Freundlich isotherm model. The kinetic analysis of WB, SDS-mWB, and CTAB-mWB revealed that the pseudo-second-order kinetic model provides a thorough explanation for each of these adsorbents. It was found that CTAB-mWB can preferably be used for the removal of chromium(vi) due to its high affinity with adsorbate molecules and adsorption capacity.

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1. Introduction

Due to the limited amount of naturally occurring water resources, water pollution is a more difficult and significant problem than any other type of environmental issue. Due to the unavailability of the latest technologies for waste-water treatment, most of the under-developing and poor nations are at high risk. Numerous different forms of contaminants are poisoning the water supplies, harming aquatic life and threatening the availability of recreational water.¹ Heavy metals are highly dangerous, non-biodegradable and environment persistent pollutants as compared to other pollutants. These metals pollute water resources from both anthropogenic and natural sources. Nowadays, researchers are focusing on health risks brought by heavy metal contamination.^{2,3}

There are different sources of contaminants that pollute the water, such as municipal waste, mining, present-day farming practices, marine discard, radioactive disposal, oil spillage, underground stockpiling spillages, and industries. Out of all the above-mentioned resources the major one is industrial waste. Industrial waste may be in the form of solid, liquid, or gas, which directly discharges into the environment. Many

^aDepartment of Chemistry, Lahore Garrison University, Lahore, Pakistan

^bDepartment of Chemistry, School of Science, University of Management and Technology, Lahore, Pakistan

^cDepartment of Chemistry, School of Natural Sciences (SNS), National University of Science and Technology (NUST), H-12, Islamabad, 46000, Pakistan. E-mail: shahidgcs10@yahoo.com

^dDepartment of Chemistry, College of Science, Princess Nourah bint Abdulrahman University, P. O. Box 84428, Riyadh 11671, Saudi Arabia

^ePINSTECH, Nilore, Islamabad, Pakistan

^fDepartment of Chemistry, COMSATS University, Abbottabad, Pakistan

^gDepartment of Pharmaceutics, College of Pharmacy, Umm Al-Qura University, Makkah 21955, Saudi Arabia

^hDepartment of Pharmaceutics and Industrial Pharmacy, Faculty of Pharmacy, Minia University, Minia 61519, Egypt

ⁱDepartment of Pharmaceutical Sciences, College of Pharmacy, AlMaarefa University, Riyadh 13713, Saudi Arabia

^jChemistry Department, Faculty of Science, King Khalid University, P. O. Box 9004, Abha 61413, Saudi Arabia

^kBiology Department, Faculty of Science, King Khalid University, P. O. Box 9004, Abha 61413, Saudi Arabia

^lDepartment of Semi Pilot Plant, Nuclear Materials Authority, P. O. Box 530, El Maadi, Egypt


industries (*i.e.* tanning, oil, pharmaceuticals, textile, sugar mill, soap or detergent units, paint and pigments, electroplating units, and fertilizers) discharge numerous toxic chemicals directly into the water, which cause severe effects on flora and fauna.^{4–7}

Small amounts of heavy metals cause some organic processes, while in bulk these become highly toxic. As these are non-biodegradable and pile up at different trophic levels *via* the food chain and harm human health. These metals multiply the health risk when entered into the human body or accumulate in living tissues. Few of these metals cause only physical distress while others may cause hazardous diseases or may harm the vital body system. Therefore, it is essential to minimize the release of these metals into the environment.⁸

Chromium has much importance as compared to all other heavy metals, and both of its oxidation forms (Cr(III) and Cr(VI)) are used chiefly in electroplating, leather tanning, metallurgy, paint and pigments, wood preservatives, dyeing, textile, and steel manufacturing. Out of both its oxidation forms, hexavalent form (*i.e.* Cr(VI)) is one of the unwanted heavy metals as it badly affects human health *via* accumulating in the food chain and causing different diseases.^{9–11} Salts of chromium are mostly utilized for tanning purposes, trivalent chromium sulfate ($[\text{Cr}(\text{H}_2\text{O})_6]_2(\text{SO}_4)_3$) is one of the most effective and efficient tanning agents.^{12,13} It was reported that the samples of groundwater from a few districts of Pakistan demonstrated chromium contents in the range from <0.001 to 9.8 mg L^{-1} , the samples of well water collected from Kasur (local area), Punjab province showed maximum results *i.e.* 2.12 mg L^{-1} ,¹⁴ though the samples of surface water collected from Bara River (Nowshera), KPK province showed the results in 0.16 – 0.29 mg L^{-1} range.¹⁵ These findings reflect that industrial wastewater may affect the quality of water. With a few exemptions,^{16,17} the majority of findings show that the chromium contents in soil are present within the tolerable range of 100 – 150 mg kg^{-1} , and the average amount of the chromium in world soil has been built up to 60 mg kg^{-1} .⁹

Diverse techniques, including photocatalysis, membrane separation, biological oxidation, ozonation, adsorption, ion-exchange, oxidation, reverse osmosis, ultra-filtration, electro-dialysis, and electrochemical approaches, have been used to remove colours and trace metals from wastewater.^{18–22} All of the above-mentioned methods are not very useful because these are best for the isolation of high contents of trace metals from wastewater while not much effective for trace amounts of metals. Some other disadvantages of these methods are partial removal of metals, dependence on pH change, costly hardware and checking framework prerequisites, high energy or reagent necessities, and production of poisonous waste materials that need disposal.^{23–27} Furthermore, these methods might be ineffectual or incredibly costly when metal contents in wastewater approach the range of 1 – 100 ppm .²⁸

The utilization of biomass for the removal of metal is viewed as a suitable option in contrast to conventional methods. Biosorption of trace metals is described as the utilization of biomass for the extraction of trace metals from wastewater *via* metabolically mediated or physicochemical adsorption of

metal.²⁹ The very important characteristics of biosorption are low cost and highly efficient for removal of trace metals even at very low concentrations.³⁰ The most commonly used adsorbent is activated carbon. Unconventional adsorbents have been used for the removal of dyes from wastewater, including clay, calcium alginate hydrogel beads,³¹ guar gum-based hydrogels,³² wheat bran,^{33,34} walnut shell,³⁵ fly ash, microalga *Spirulina platensis*,³⁶ rice straw,³⁷ *Cucumis sativus* peel,³⁸ crop residues,³⁹ corncob, palm ash,⁴⁰ barley husk,⁴¹ *Salix babylonica* leaves powder,⁴² nanomaterials,^{43,44} and polymer particles.⁴⁵ Agricultural wastes and by-products, which are inexpensive, environmentally benign, and resource sustainable, are commonly employed for wastewater treatment.⁴⁶ Table 1 summarizes the findings of certain studies adsorption reported in the literature employed for the removal of chromium VI metal ion.

Surfactants are basically like short-chain fatty acids and have both hydrophilic and hydrophobic characteristics. They have both polar and nonpolar poles which show an affinity for polar and nonpolar molecules, respectively. The molecules of surfactant form a monolayer and decrease the surface tension of the medium at the interface. In some cases, they behave like a molecule that is capable of forming micelles. They are also known as surface-active agents, amphiphiles, tensides, or paraffin chain salts. Detergents are also surfactants and are used for cleaning purposes. In the aqueous condition surfactant forms two ends, one of them is known as the head (*i.e.*, hydrophilic) and the other is known as the tail (*i.e.*, hydrophobic). They are sorted into different classes *e.g.*, cationic (*i.e.*, trimethyl dodecyl ammonium chloride, lauryl amine hydrochloride, cetyltrimethylammonium bromide), anionic (*i.e.*, sodium stearate, sodium dodecylbenzene sulfonate, sodium dodecyl sulfate), non-ionic (*i.e.* polyoxyethylene alcohol, polysorbate 80, alkylphenol ethoxylate, propylene oxide-modified polydimethylsiloxane) and zwitterionic (*i.e.* coco amido-2-hydroxypropyl sulfobetaine, dodecyl betaine, lauramidopropyl betaine). CTAB and SDS are the most frequently used cationic and anionic surfactants, respectively.⁴⁷

The objective of this study is to evaluate the removal efficiency of metal ions using a low-cost adsorbent *i.e.*, wheat bran and its modified forms. Surface modification of wheat bran was done using cationic and anionic surfactants. Surfactants being amphiphilic structures and owing to their surface properties are expected to enhance the surface area of the used adsorbent. In this work, a comparison will be made between the adsorbent and its modified forms in terms of the percentage extraction of metal ions following batch adsorption studies. Several parameters like the effect of temperature, pH, adsorbate amount, and contact time were considered. From data obtained, isotherms, kinetic models, and thermodynamics were also evaluated.

2. Materials and methods

2.1 Preparation of adsorbents

The wheat (*Triticum aestivum*) bran is an agricultural waste obtained from flour milling in Abdul Hakim (Village), Punjab, Pakistan). The collected adsorbent was firstly washed with double-distilled water, dried in a calibrated oven at



Table 1 Summary of various adsorbents used for chromium(vi) removal

Adsorbent	Time [h]	pH	T [°C]	Cr(vi) [mg L ⁻¹]	Dose [g L ⁻¹]	Adsorption capacity [mg g ⁻¹]	Ref.
Low cost adsorbent	Rice straw	2-6	27	100	10	3.2	48
	Saw dust	1-10	30	20-1000	2-24	16	48
	Charcoal	1-10	30	20-1000	2-24	17	48
	Kaolinite	4.6	25	4.6	2000	6.1	49
	Red clay	4-6	—	0.46	40	1.3	50
	Rice straw	1.5	2-6	100	10	3.2	48
	<i>Sargassum dentifolium</i>	1.0	7	100	1500	41.2	51
	<i>Exiguobacterium</i> sp. ZM-2	2.0	2.5	100	—	29.8	52
	<i>Saccharomyces cerevisiae</i> and <i>Rhizobium</i>	3	2	50	—	24-31	53
	<i>Aspergillus niger</i>	—	2	40	200	97.1	54
Carbon NM's	Low cost activated carbon	3.5	25	—	1	74.63	55
	Graphene oxide	3.0	25	—	—	49	56
	MWCNT's	2.0	25	—	2-6	23-32	57
	Ag ₂ O/saw dust nanocomposites	3	25	25-100	—	60.24	58
	HD/IMA-modified zeolites erionite	7	2	200	0.1 g/50 mL	0.103	59
Surfactant modified zeolites	HD/IMA-modified zeolite cowlesite	7	25	200	0.1 g/50 mL	0.763	60
	HD/IMA-modified clinoptilolite	7	15	200-600	20 mg/10 mL	0.124	61
	ODA-modified clinoptilolite	—	7	500	20 mg/10 mL	54	61

a temperature of 60 °C for 12 h and then cooled in the air-tight desiccator for about 20–30 min. Dried WB was ground to a particle size of 80–100 mesh.⁶²

2.1.1 Preparation of modified wheat bran. The obtained unmodified WB was separately treated with solutions of surfactants (SDS and CTAB) using surfactant concentration 1 mmol L⁻¹. The mixture was stirred at a magnetic plate for 24 h at 30 °C with a ratio of WB (1 g): surfactant solution (50 mL). The sample was filtered after the 24 hours were up and washed three times with double-distilled water to get rid of the unreacted surfactant components. The resulting residue was dried at 60 °C for 12 hours. Glass vials that were airtight used to keep the dry powder. The produced adsorbent materials' functional groups were examined using an FTIR Spectrophotometer (Bruker-Model Alpha).

2.2 Sorption studies

Three adsorbents, wheat bran, CTAB modified wheat bran, and SDS modified wheat bran, were used in batch sorption experiments to assess the percentage removal of chromium VI in aqueous solution. For the sorption experiments, a dissolution tester (Galvano Scientific, BETA-8L) and magnetic hot plate (Cacao 78-1, China) were employed. A combination of factors, including adsorbate concentration (2.5–12.5 ppm), adsorbent dose (1–6 g), pH effect (2–12), agitation time (15–240 min), and agitation speed (50–300 rpm), were studied in the sorption studies. Each combination was sampled after the pre-determined amount of time and filtered using whatmann filter paper. Adsorbent dosage (5 g/100 mL), temperature (30 ± 2 °C), pH (4), contact period (1 h), and speed (150 rpm) were all used in the adsorption isotherm studies, while the concentration of the chromium solution was changed from 2.5–12.5 ppm.

Adsorption isotherm study for the adsorption of chromium(vi) metal ions was done by varying the adsorbate concentration from 2.5 to 12.5 ppm, while other parameters including adsorbent dosage (5 g/100 mL), temperature (30 ± 2 °C), pH (4), contact time (1 h), and speed (150 rpm) were kept constant. Kinetic tests at various time intervals *i.e.*, 15–240 min were conducted keeping all other set of conditions the same. By using a UV-VIS spectrophotometer (Shimadzu, UV1800) set at 350 nm, the residual concentration of chromium(vi) in the samples was determined. The total % elimination of metal ions was determined using eqn (1).

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

where C_0 (mg L⁻¹) is the initial chromium(vi) concentration and C_t (mg L⁻¹) is the equilibrium chromium concentration.

3. Results and discussion

3.1 Properties of the adsorbents

The characterization of all adsorbents including WB, SDS-mWB, and CTAB-mWB was done by FTIR. Three different infrared spectra have been obtained that help to identify the attached functional groups. The infrared spectra of WB, SDS-



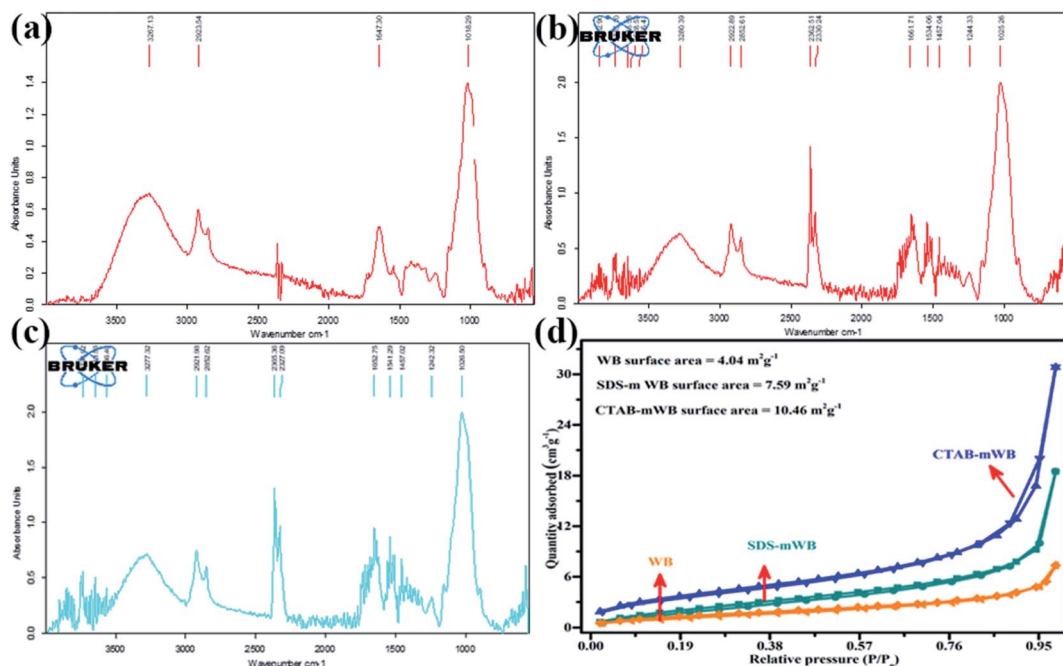


Fig. 1 FTIR spectra for modified and unmodified wheat bran (a) WB, (b) SDS-mWB, (c) CTAB-mWB and (d) the BET surface area isotherms are calculated using the adsorption–desorption of N₂ using WB, SDS-mWB and CTAB-mWB.

mWB, and CTAB-mWB are shown in Fig. 1(a)–(c) respectively. WB biosorbent showed the number of peaks in the infrared region (*i.e.*, 500 to 4000 cm⁻¹). The peak showed on 1018.29 cm⁻¹ may be due to the presence of the (C–O–C) functional group. The peak at 1247.16 cm⁻¹ represents the –COOH stretching of organic compounds (*i.e.*, carboxylic acid). The strong CH₂ asymmetric distortion appears at 1412.40 cm⁻¹ while asymmetric C=C stretching occurs at 1542.58 cm⁻¹. The peaks at 1647.30–1733.50 cm⁻¹ are stretching of C=O stretching. The C–H stretching appears at 2853.38 and 2923.54 cm⁻¹, while the stretching of the O–H group occurs at 3267.13 cm⁻¹ (ref. 63) (see Fig. 1(a)).

But in the case of SDS-mWB the more intense peak showed at 1025.26 cm⁻¹ which represents the OSO₃⁻ symmetric stretching. While the peaks at 1244.33, 1457.04, 1534.06, 1661.71, 2852.61–2922.89 cm⁻¹ showed –COOH (stretching), –CH₂ (asymmetric distortion), C=C (stretching), C=O (stretching), and C–H (stretching) respectively.⁶⁴ The increase in the intensities of peaks is due to high concentration involving functional groups, and the change in wavenumber causes the conversion of the hydrophilic nature of adsorbent to hydrophobic. This is because the water molecules attached to the surface of surfactant are replaced by hydrated cations.⁴⁴ While the peak of O–H stretching (*i.e.*, at 3280.39 cm⁻¹) for adsorbent SDS-mWB showed the same intensity as that of WB (see Fig. 1(b)). It can be concluded that these sulfate groups (*i.e.*, OSO₃⁻) of SDS-mWB will affect the adsorption process. While the CTAB-mWB showed the more intense but identical peaks as that was obtained for WB (see Fig. 1(c)). Similar to the SDS-mWB, an increase in wavenumber was observed representing its hydrophobic nature.⁴⁴ The calculated BET surface areas for

WB, SDS-mWB and CTAB-mWB were, respectively, 4.04, 7.59 and 10.46 m² g⁻¹ (Fig. 1(d)). The surface areas of SDS-mWB and CTAB-mWB are higher than that of WB.

3.2. Batch adsorption study

3.2.1. Effect of adsorbate amount. Variable starting chromium levels were used to investigate the influence of adsorbate concentration on the adsorption of chromium(vi) ions from aqueous solution (2.5, 5.0, 7.5, 10.0 and 12.5 ppm). Fig. 2 depicts the influence of adsorbate concentration on chromium removal by WB, SDS-mWB, and CTAB-mWB. The individual results of WB, SDS-mWB and CTAB-mWB showed that the

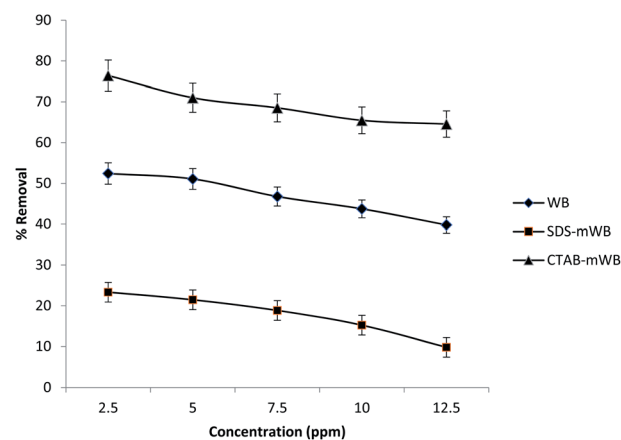


Fig. 2 Effect of adsorbate amount on the sorption of chromium ions (pH = 4; adsorbent dose = 5 g/100 mL; agitation speed = 150 rpm; temp = 30 ± 2 °C; contact time = 1 h).



adsorption of chromium ions is continuously going on decreasing with the increase in adsorbate amount, a similar effect was reported by Nameni.⁶⁵ In case of a lower concentration of adsorbate, more active sites will be available and the possibility of contact of HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ ions will be maximum. But on increasing the adsorbate amount the availability of contact surface will be decreased, and there are also the chances of repulsion by already attached metal ions.^{65,66} On comparing the results of all three samples the order of chromium adsorption is $\text{CTAB-mWB} > \text{WB} > \text{SDS-mWB}$ (76.4% > 52.4% > 23.3%) at initial concentration 2.5 ppm. As we know the CTAB-mWB is cationic therefore it shows a better result as compared to WB and SDS-mWB. And SDS-mWB (anionic-modified adsorbent) showed the adsorption efficiency even less than WB, this may be due to repulsion between already attached anions at contact surface and introducing chromium(vi) metal ions.⁶⁷

3.2.2. Effect of adsorbent dosage. The impact of adsorbent dosage on the removal of $\text{Cr}(\text{vi})$ metal ions from aqueous solution has been determined under ideal conditions with a constant pH of 3 and various adsorbent doses (1.0, 2.0, 3.0, 4.0, 5.0, and 6.0 g/100 mL). The impact of adsorbent dose on the removal of chromium using WB, SDS-mWB, and CTAB-mWB is shown in Fig. 3. Individual WB and CTAB-mWB data revealed that the clearance percent steadily rose as the adsorbent dosage was increased. This is due to the presence of more active sites that increase with the adsorbent dosage and the probability of contact of HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ ions on adsorbent particles increases consequently the removal efficiency of chromium ions increases.^{65,68} However, as the adsorbent dosage is increased, the removal effectiveness of SDS-mWB decreases. Because of the negative charges (SO_4^-) that are present on the surface of the adsorbent, SDS is known to be an anionic surfactant. The concentration of surfactant SDS will be increased with the increase of adsorbent dose, therefore the negative charges on the adsorbent surface will hinder the attachment of HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ ions thus the adsorption efficiency will be decreased.⁶⁷ The maximum removal for $\text{Cr}(\text{vi})$ on WB, SDS-mWB, and CTAB-mWB adsorbents was found to be

77.6%, 24.5%, and 95.4%, respectively (see Fig. 3). If we compare the results of WB, SDS-mWB, and CTAB-mWB then it can be seen that CTAB-mWB is a highly efficient adsorbent. As we know the CTAB is a cationic surfactant and produces a positive charge on the surface of the adsorbent therefore the tendency of the adsorbent to attract the anions (HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$) will be increased.⁶⁹

3.2.3. Effect of agitation time. For the investigation of the contact time effect on the adsorption of $\text{Cr}(\text{vi})$, the adsorbent samples (including WB, SDS-mWB, and CTAB-mWB) were taken into the separate flasks with an adsorbent dosage of 5 g in 100 mL of 5 ppm chromium solution at fix pH 3.0, temperature $30 \pm 2^\circ\text{C}$, and speed 150 rpm. The effect of agitation time was noted at a series of intervals (15, 30, 45, 60, 120, 180, and 240 min) by measuring the absorbance value of filtered samples. The variation in percentage removal of $\text{Cr}(\text{vi})$ metal ions with the time of contact has been shown in Fig. 4. All three adsorbents WB, SDS-mWB, and CTAB-mWB showed maximum percentage removal of $\text{Cr}(\text{vi})$ at a time of 240 min, which was equal to 79.0%, 27.0%, and 98.7%, respectively. Fig. 4 illustrated that the removal efficiency of chromium for all the samples (WB, SDS-mWB, and CTAB-mWB) initially increased rapidly within 60 min (*i.e.*, 1 h) and after this, no significant changes occur. The equilibrium will be established after 60 min, similar results were reported by Nameni.⁶⁵

3.2.4. pH effect. The impact of pH on the adsorption process is more critical than the effects of other parameters. For the investigation of the pH effect on the adsorption of $\text{Cr}(\text{vi})$, the adsorbent samples (*i.e.*, WB, SDS-mWB, and CTAB-mWB) were taken into the separate flasks with an adsorbent dosage of 5 g in 100 mL of 5 ppm chromium solution at fix conditions temperature $30 \pm 2^\circ\text{C}$, and speed 150 rpm. By adjusting the pH (2, 4, 6, 8, 10, and 12) and evaluating the absorbance of filtered samples, the impact of pH was investigated. The pH was maintained using a 0.1 M HCl and 0.1 M NaOH solution. The experimental data of this effect is given in Fig. 5 and 6. The obtained results of WB and CTAB-mWB showed that the adsorption efficiency of chromium metal ions is inversely proportional to the pH of chromium solution. At lower pH = 2 both WB and CTAB-mWB

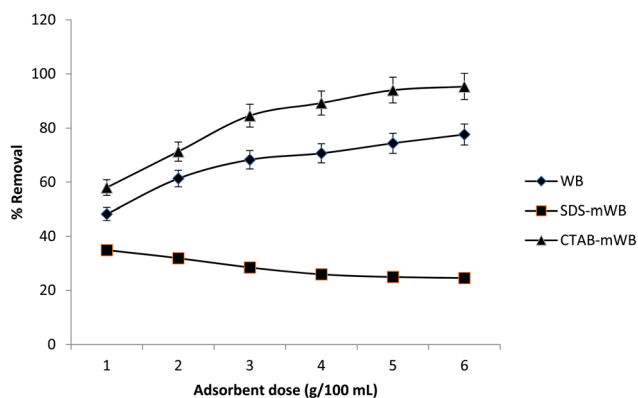


Fig. 3 Effect of adsorbent dose on the sorption of chromium ions (pH = 3; initial Cr conc. = 5 ppm; agitation speed = 150 rpm; temp = $30 \pm 2^\circ\text{C}$; contact time = 2 h).

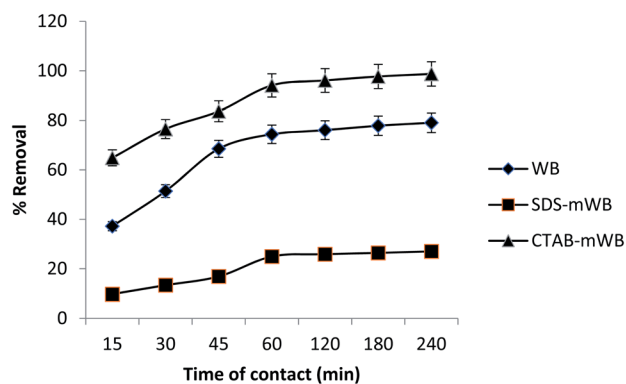


Fig. 4 Effect of contact time on the sorption of chromium ions (pH = 3; adsorbent dose = 5 g/100 mL; initial Cr conc. = 5 ppm; agitation speed = 150 rpm; temp = $30 \pm 2^\circ\text{C}$).



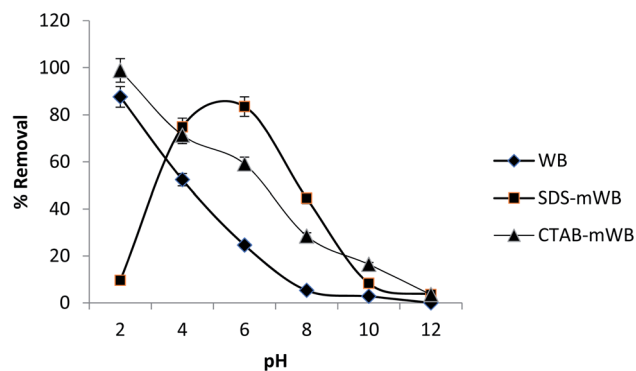
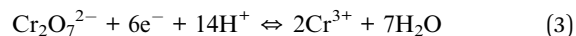
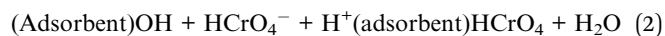


Fig. 5 Effect of pH on the sorption of chromium ions (adsorbent dose = 5 g/100 mL; initial Cr conc. = 5 ppm; agitation speed = 150 rpm; temp = 30 ± 2 °C; contact time = 1 h).

showed maximum percentage removal for chromium metal ions equal to 87.6% and 98.8%, respectively. But with the increase in the pH the adsorption efficiency of both (*i.e.*, WB and CTAB-mWB) decreased drastically. The decline in adsorption efficiency may be caused by a weakening of the electrostatic contacts between the oppositely charged adsorbent and adsorbate.⁷⁰ As the removal of Cr(vi) varies to pH, and at lower pH HCrO_4^- ion appears as the leading specie over H_2CrO_4 , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ ions. At lower pH, the hydroxyl ions (OH^-) that are present at the adsorbent surface are easily replaced by the HCrO_4^- ions (see eqn (3)).^{65,71}

The SDS-mWB showed maximum percentage removal for chromium metal ions (74.87–83.5%) at pH = 4–6. Because at

acidic pH the $\text{Cr}_2\text{O}_7^{2-}$ ions will be converted into the Cr^{3+} ions (see eqn (4)) which will be strongly attracted toward the anionic surface of SDS-mWB. The adsorption efficiency of SDS-mWB is decreased before pH 4, due to the excess of a proton (H^+) as compared to chromium metal ion (Cr^{3+}). At pH 4–6 (less acidic), Cr^{3+} ions become dominant over protons (H^+) and attracted toward the anionic surface of SDS-mWB, therefore maximum removal will occur.⁷² But at pH greater than the 6 the surface of SDS-mWB becomes more anionic which will strongly hinder the HCrO_4^- , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ ions. Therefore, the SDS-mWB will show minimum results for chromium removal.



3.2.5. Effect of agitation speed. To estimate the impact of agitation speed on the extraction of Cr(vi) ions, the adsorbent samples (including WB, SDS-mWB, and CTAB-mWB) were taken into the separate flasks with fix adsorbent dosage of 5 g in 100 mL of 5 ppm chromium solution under constant temperature 30 ± 2 °C and pH 3.0 for the contact time 60 min (*i.e.* 1 h). The study of the speed effect on adsorption of Cr(vi) was carried out at different speeds (50, 100, 150, 200, 250 and 300 rpm). Fig. 7 shows the gradual increase in adsorption rate with the increase in agitation speed, but optimal results were obtained at 150 rpm. The overall results showed that the adsorbents WB, SDS-mWB, and CTAB-mWB give the maximum adsorption results of 74.5%, 24.9% and 93.9%, respectively. Above 150 rpm,

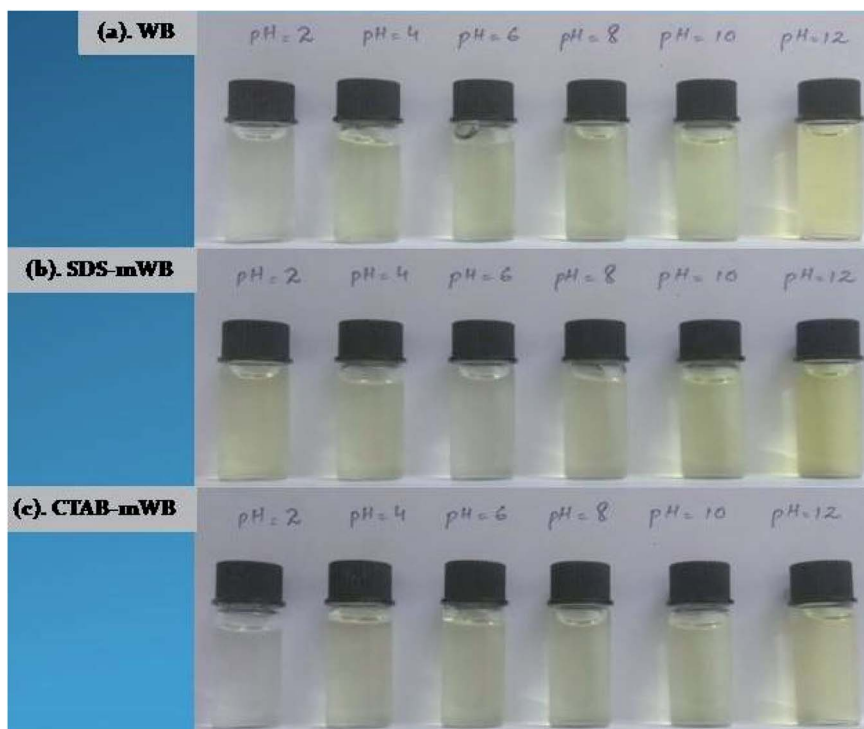


Fig. 6 Effect of pH on adsorbents, (a) WB, (b) SDS-mWB (c) CTAB-mWB.



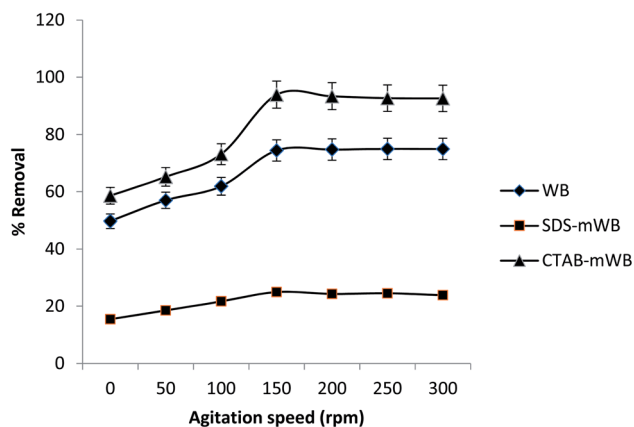


Fig. 7 Effect of agitation speed on the sorption of chromium ions (adsorbent dose = 5 g/100 mL; initial Cr conc. = 5 ppm; pH = 3.0; temp = 30 ± 2 °C; contact time = 1 h).

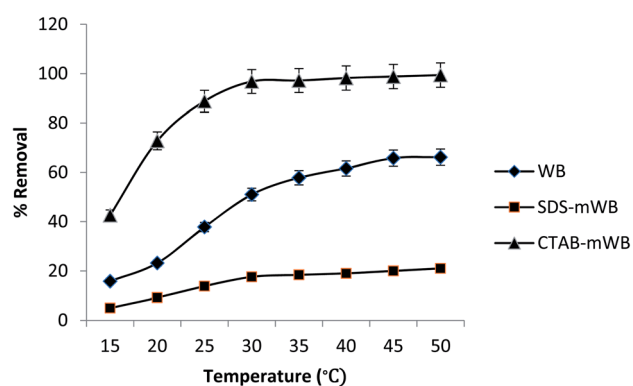


Fig. 8 Effect of temperature on the sorption of chromium ions (adsorbent dose = 5 g/100 mL; initial Cr conc. = 5 ppm; pH = 3.0; agitation speed = 150 rpm; contact time = 1 h).

a negligible change in results was observed and the equilibrium was attained. The decrease in thickness of the boundary layer surrounding the adsorbent particles causes the removal percentage to increase with agitation speed.⁷³

3.2.6. Effect of temperature. The impact of temperature on the adsorption of aqueous Cr(VI) metal ions by adsorbents (*i.e.*, WB, SDS-mWB, and CTAB-mWB) was carried out at varying the temperature from 15 to 50 °C with a constant adsorbent dosage of 5 g in 100 mL of 5 ppm chromium solution, speed 150 rpm, pH 3.0 for contact time 60 min (1 h). The experimental data obtained for all adsorbents show that a significant increase in removal capacities will occur with the increase in the temperature up to 30 °C (see Fig. 8). After 30 °C, there is no significant increase in the percentage removal of all adsorbents was observed and above this temperature, the equilibrium was established. At 50 °C temperature WB, SDS-WB, and CTAB-WB showed maximum percentage removal equal to 66.2%, 21.0%, and 99.4%, respectively. The swelling action within the internal structure of the adsorbent may cause this increase in adsorption with temperature, allowing the big molecules of chromium to penetrate further. Increased temperature may result in more adsorbate–adsorbent interaction when chromium metal ions are removed.⁷⁴

3.3. Isothermal analysis

The isothermal analysis of adsorbents (*i.e.* WB, SDS-mWB, and CTAB-mWB) was carried out by the estimation of the characterization and removal capacity of adsorbents by taking the help of a series of various isothermal analyses done by researchers.^{44,65,67} The equilibrium data was applied to both Langmuir (eqn (5)) and Freundlich equation (eqn (6)). The Langmuir model assumes that the adsorption of chromium ions will take place on a uniform monolayer of $-\text{OH}^-$ ions present on the surface of unmodified wheat bran (WB) and there will be no interaction between adsorbed ions (Fig. 9).

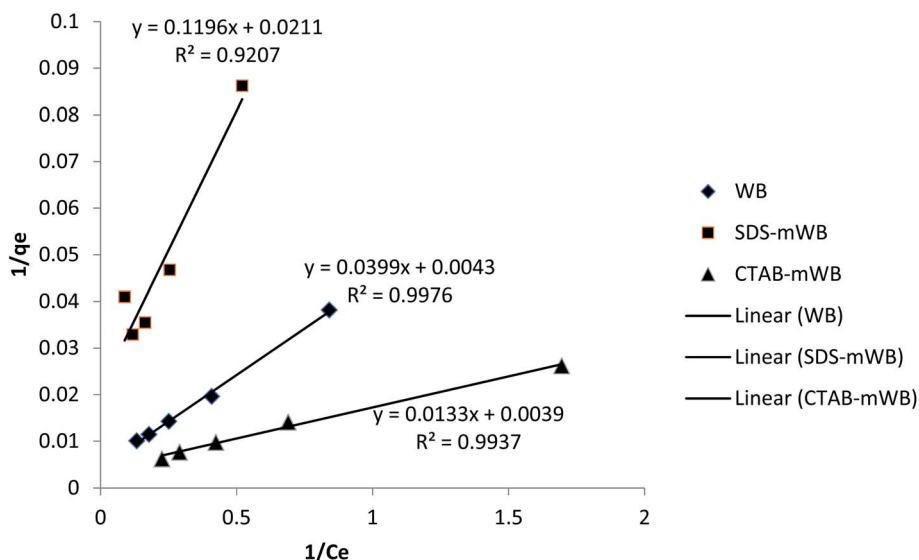


Fig. 9 Test of nature of adsorption by Langmuir adsorption isotherm.



Similar behavior was shown in the case of SDS-mWB, but in this case, the monolayer of sulfate group ($-\text{SO}_3^-$) of anionic surfactant will be responsible for the adsorption of chromium metal ions (Cr(III)) as discussed in the effect of pH on adsorption. The mathematical expression for the Langmuir isotherm is given below;⁶⁵

$$1/q_e = 1/bq_{\text{max}}1/C_e + 1/q_{\text{max}} \quad (4)$$

where q_{max} is the maximum quantity of adsorbate that may be absorbed per unit dry weight of sorbent, b is the empirical constant that characterizes the affinity of sorbent to sorbate, adsorbate's equilibrium concentration is known as C_e , and its equilibrium quantity of adsorbed material is known as q_e .

The mathematical expression for the Freundlich isotherm is given below.

$$\log q_e = \log K_f + 1/n \log C_e \quad (5)$$

where q_e is the adsorbed chromium quantity (experimental value), C_e is residual chromium concentration, K_f is the Freundlich constant, related to sorption capacity of adsorbent, and $1/n$ is the Freundlich isotherm constant related to adsorption intensity. The values of K_f and n were obtained by plotting the graph between $\log q_e$ versus $\log C_e$ (Fig. 10). K_f value was calculated from the intercept, while the value of n was estimated from the slope.

The plot of the Freundlich model showed that the cationic modified wheat bran (CTAB-mWB) will follow the Freundlich

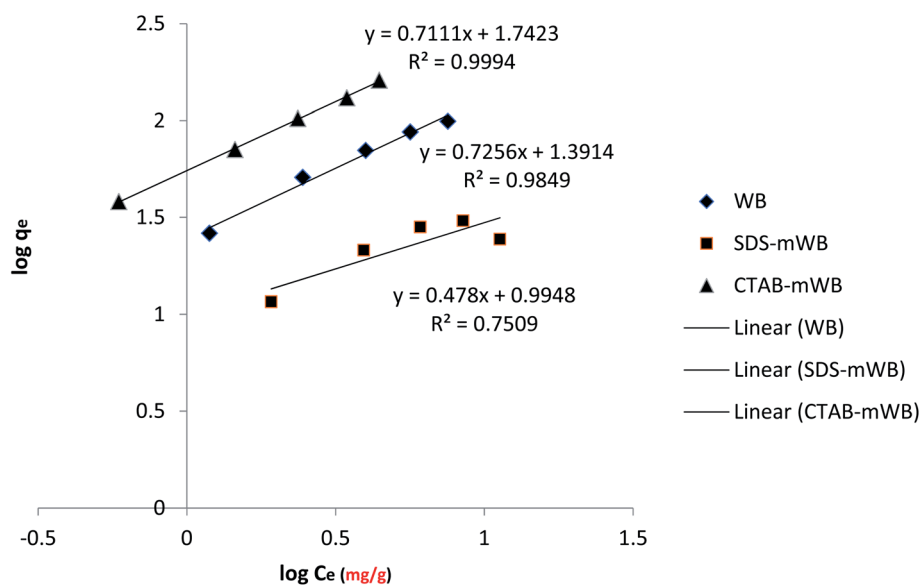


Fig. 10 Test of nature of adsorption by Freundlich adsorption isotherm.

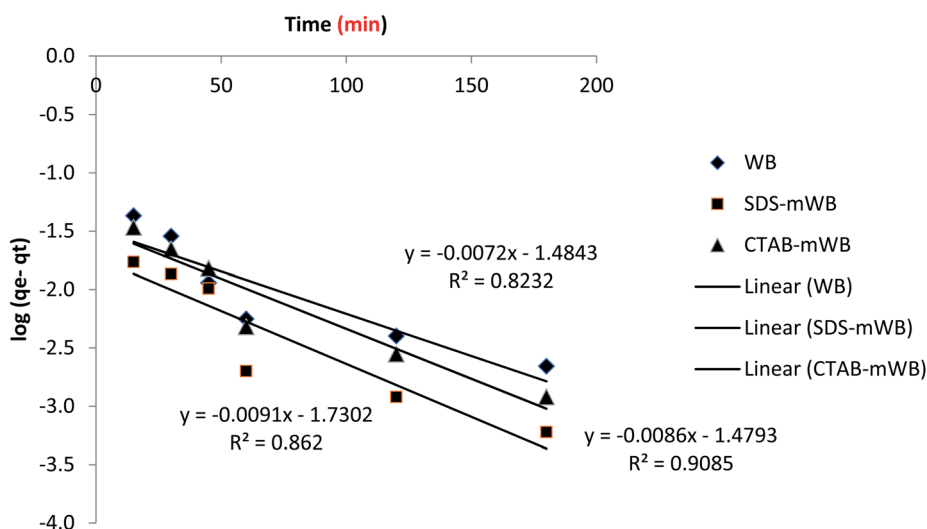


Fig. 11 Graph of pseudo-first order.



isotherm with a suitable correlation factor $R^2 = 0.999$ and the value of n is 1.41 (Fig. 10). The Freundlich model assumes that the adsorption energy of chromate ions (HCrO_4^-) on the CTAB-mWB adsorbent will decrease exponentially with increasing surface saturation and the surface of the adsorbent is heterogeneous.^{75,76}

3.4. Adsorption kinetic

To verify the experimental data and identify the regulated mechanisms of the adsorption process, such as mass transfer and chemical reaction, first- and second-order kinetic models are utilized. All of the adsorbents (including WB, SDS-mWB, and CTAB-mWB) were tested at various intervals (15, 30, 45, 60, 120, 180, and 240 minutes) with the adsorbent dosage of 5 g

in 100 mL of 5 ppm chromium solution of pH 3.0, temperature 30 ± 2 °C, and speed 150 rpm held constant. The obtained experimental data is then applied to the pseudo-first equation (Lagergren's equation)⁶⁵ and second-order equation⁷⁷ for the study of adsorption kinetic.

Pseudo first order equation (Lagergren's equation)

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t \quad (6)$$

Pseudo second order equation

$$t/q_t = 1/k_2q_e^2 + t/q_e \quad (7)$$

where q_t denotes metal uptake per unit weight of adsorbent (mg g^{-1}) at time t , q_e denotes metal uptake per unit weight of

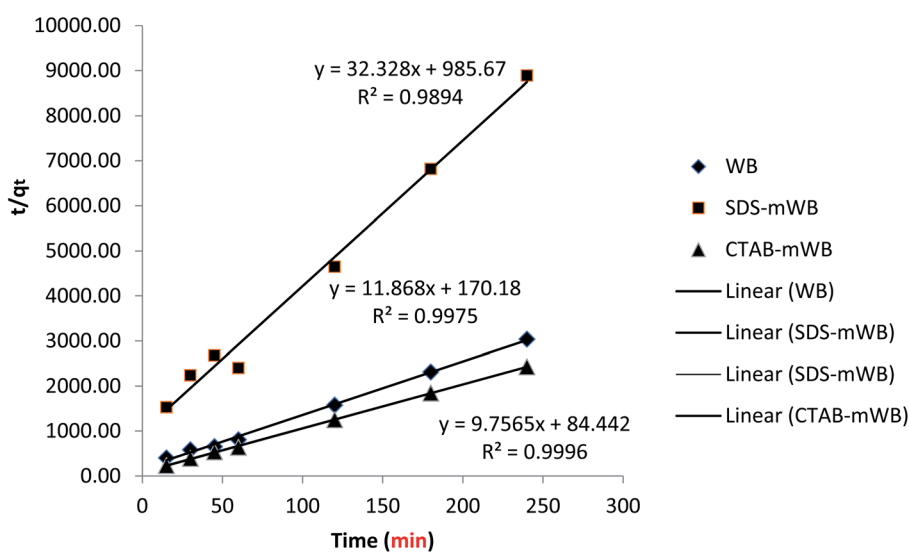


Fig. 12 Graph of pseudo second order.

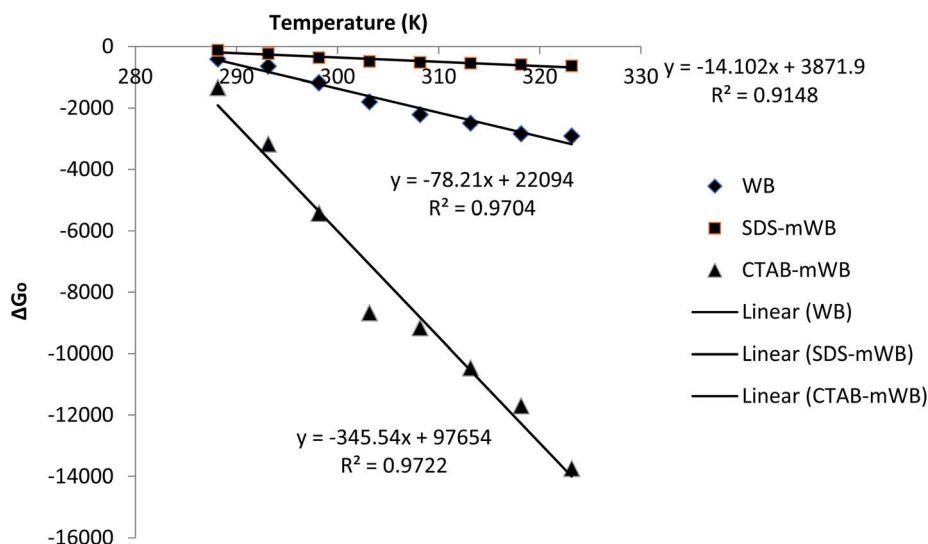


Fig. 13 Thermodynamic study for adsorption of chromium(vi) by adsorbent (adsorbent dose = 5 g/100 mL; initial Cr conc. = 5 ppm; pH = 3.0; agitation speed = 150 rpm; contact time = 1 h).



adsorbent (mg g^{-1}) at equilibrium, and k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) denote the rate constants of the pseudo-first-order (Fig. 11) and pseudo-second-order kinetic equations, respectively.⁶⁵ These curves' slopes and intercepts were utilised to calculate k_1 and k_2 , as well as the equilibrium capacity (q_e). According to the findings, the adsorption process follows a pseudo second-order model. As illustrated in Fig. 12, the plot of t/q_t vs. $1/q_e$ produces a straight line.

The results of pseudo first and second order kinetics were obtained after the adsorption kinetic of all adsorbents including WB, SDS-mWB and CTAB-mWB. The equilibrium data of WB, SDS-mWB and CTAB-mWB showed that the R^2 values of WB, SDS-mWB and CTAB-mWB for first order kinetics and second order kinetic were 0.823, 0.862, 0.908 and 0.997, 0.989, 0.999, respectively. The value of R^2 should be closed to 1. The kinetic study showed that all the samples will follow the pseudo second order kinetic as their R^2 values are very close to 1.

3.5. Thermodynamic study

Thermodynamic study for the adsorption of aqueous Cr(vi) metal ions on adsorbents (*i.e.*, WB, SDS-mWB, and CTAB-mWB) was conducted by varying the temperature from 15 to 50 °C at constant adsorbent dosage 5 g in 100 mL of 5 ppm chromium solution, speed 150 rpm, pH 3.0 for contact time 60 min (1 h).

$$\Delta G_0 = \Delta H_0 - T\Delta S_0 \quad (8)$$

The fact that ΔG_0 is negative denotes that adsorption is spontaneous.⁷⁸ The value of the adsorption capacity will be greater at a higher temperature since G_0 increases as the temperature rises. The positive value of ΔH_0 denotes that adsorption is endothermic, and the positive value of ΔS_0 denotes that the adsorbents have a favorable affinity for the chromium solution.⁶⁵ By comparing the values of ΔS_0 for all adsorbents (*i.e.*, WB, SDS-mWB, and CTAB-mWB), it can be concluded that the order of adsorbent-adsorbate affinity is CTAB-mWB > WB > SDS-mWB (345.5 > 78.21 > 14.10) (Fig. 13).

3.6. Adsorption mechanisms

Normally adsorbate-adsorbent interaction is caused by various factors including ionic exchange, electrostatic interaction, and hydrogen bonding. It was observed (Fig. 14) that the unmodified wheat bran (*i.e.*, WB) shows the maximum adsorption capacities at optimum adsorption conditions (*i.e.* adsorbent dosage 5 g, adsorbate concentration 5 ppm, pH 2, speed 150 rpm, temperature 30 ± 2 °C, contact time 60 min). A homogeneous monolayer of hydroxyl groups is present on the surface of wheat bran. At a more acidic pH (*i.e.*, 2), the $-\text{OH}^-$ ions will be replaced with HCrO_4^- (which are more dominant in acidic conditions) by this the chromium adsorption efficiency will be increased. The adsorption of chromium by WB will follow the Langmuir isotherm. The adsorption reaction between adsorbent and adsorbate will be spontaneous and endothermic. The kinetic study showed that the adsorption reaction will be pseudo-second order. The excess number of the

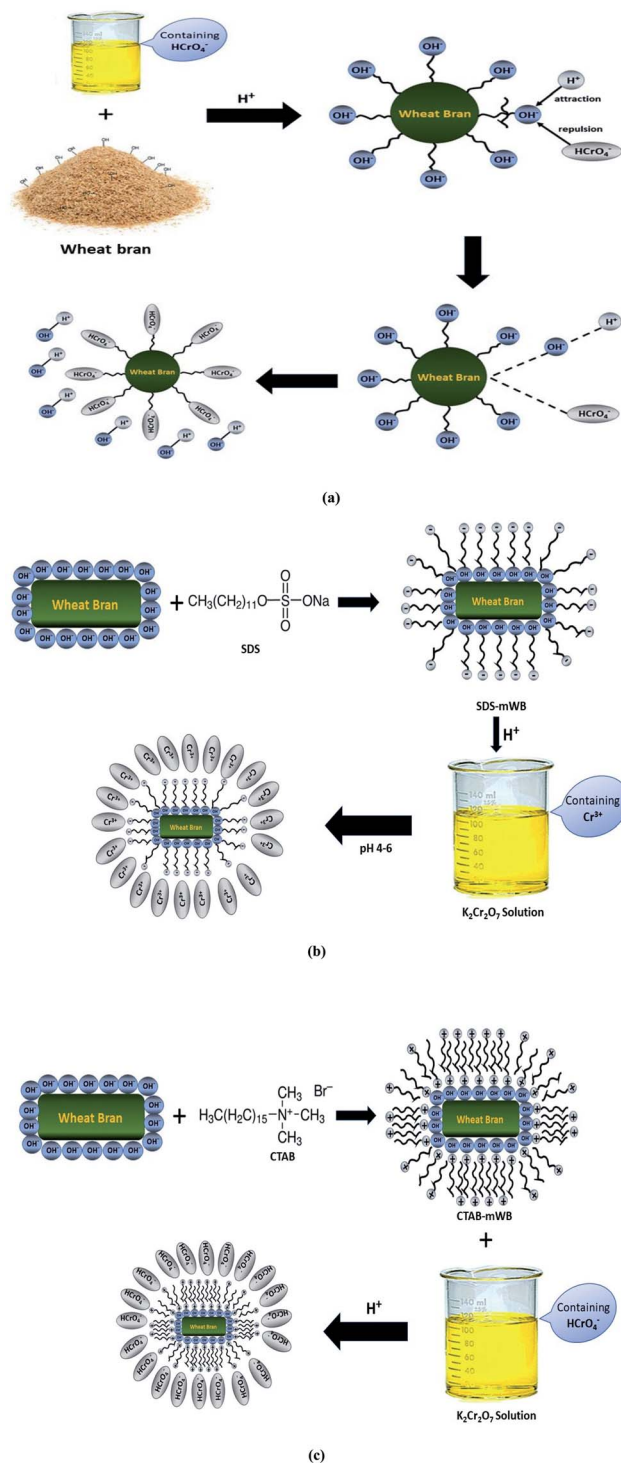


Fig. 14 Adsorption mechanism for the removal of Cr(vi) by adsorbent (a) WB, (b) SDS-mWB and (c) CTAB-mWB.

proton (H^+) will attract the hydroxyl groups of WB and at the same time HCrO_4^- ions will repel the $-\text{OH}^-$ by electrostatic forces of attraction and repulsion, respectively (see eqn (3)).

The adsorption study of SDS modified wheat bran SDS-mWB (anionic adsorbent) showed that the maximum removal of chromium will occur at optimum adsorption conditions (*i.e.*,



adsorbent dosage 5 g, adsorbate concentration 5 ppm, pH 4–6, speed 150 rpm, temperature 30 ± 2 °C, contact time 60 min). As sulphate groups ($-\text{SO}_4^-$) of SDS form a homogenous monolayer on WB and follow the Langmuir isotherm model. At suitable acidic pH (*i.e.*, 4–6), the sulphate ions ($-\text{SO}_4^-$) will attract the Cr^{+3} ions (which are more dominant at pH 4–6) by strong forces of attraction (see eqn (4)). The kinetic study of SDS-mWB showed that the adsorption reaction will follow the pseudo-second order. In the case of SDS-mWB adsorption reaction between adsorbent and adsorbate will be spontaneous and endothermic.

The adsorption study of CTAB modified wheat bran CTAB-mWB (cationic adsorbent) showed that the maximum removal of chromium will occur at optimum adsorption conditions (*i.e.*, adsorbent dosage 5 g, adsorbate concentration 5 ppm, pH 2, speed 150 rpm, temperature 30 ± 2 °C, contact time 60 min). As trimethylamine groups ($-\text{N}^+(\text{CH}_3)_3$) of CTAB form a heterogeneous monolayer on WB and follow the Freundlich isotherm model. At a more acidic pH (<3), the trimethylamine ions ($-\text{N}^+(\text{CH}_3)_3$) will attract the HCrO_4^- ions (which are more dominant at pH < 3) by strong forces of attraction (see eqn (3)). The adsorption reaction between adsorbent and adsorbate will be spontaneous and endothermic. The kinetic study of CTAB-mWB showed that the adsorption reaction will follow the pseudo-second order.

4. Conclusion

In a batch system, WB, SDS-mWB, and CTAB-mWB were used to adsorb chromium metal from an aqueous solution. The initial chromium content, pH, agitation time, adsorbent dose, temperature and agitation speed were all varied to better understand the adsorption mechanism. The removal efficiency of WB and CTAB-mWB declined with increasing chromium concentration and increased with increasing adsorbent dosage, according to the results of the experiments. With increasing starting chromium concentration and adsorbent dosage, SDS-mWB removal effectiveness dropped. The optimum pH for chromium removal by WB and CTAB-mWB is 2, while for SDS-mWB the suitable pH is between 4 and 6. Agitation time of 240 min The adsorption value of chromium was also related to the agitation speed and temperature. At agitation speed (*i.e.*, 150 rpm) and temperature (*i.e.* 25–30 °C), the adsorption results for all adsorbents reach a maximum value and attain equilibrium. The maximum result for chromium uptake was obtained as 87.7%, 83.5% and 98.8% for WB, SDS-mWB, and CTAB-mWB, respectively. The equilibrium data of WB and SDS-mWB was modeled by the Langmuir adsorption isotherm, while the data of CTAB-mWB was fitted well in the Freundlich isotherm model. The kinetic study of WB, SDS-mWB, and CTAB-mWB showed that all of these adsorbents are excellently justified by the pseudo-second-order kinetic model. And the thermodynamic study of all adsorbents confirmed the spontaneous chemical adsorption between adsorbate and adsorbent. It was found that CTAB-mWB can preferably be used for the removal of chromium due to its high affinity with adsorbate molecules and adsorption capacity.

Author contributions

Sadaf Sarfraz: conception, performed metal extraction experiments, visualization of data, writing reviewing, and editing. Safdar Ameer: material synthesis, visualization of data, writing reviewing, and editing. Mohsin Javed: conception, design of study, writing-original draft preparation and critical revision, supervision. Shahid Iqbal: design of study, performed major experimental works, writing-original draft preparation. Samar O. Aljazzar: methodology, reviewed original manuscript, and critical revision. Manzar Zahra: conducted metal extraction experiments, acquisition of data, writing-original draft preparation. Shahid Amin: analysis and/or interpretation of data, performed FTIR analysis. Khizar Hussain Shah: drafting the revised manuscript, performed adsorption analysis and critical revision. Mohammed A. S. Abourehab: conception, design of the study, acquisition of data, interpret the data. Eslam B. Elkaeed: visualization of data, reviewed the original manuscript and critical revision. Nasser S. Awwad: drafting the revised manuscript, acquisition of data, and critical revision. Hala A. Ibrahim: analysis and/or interpretation of data, performed FTIR analysis.

Conflicts of interest

The authors declare no conflict of interest.

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