Semicarbazide functionalized flax fibers for effective adsorption of Cr(VI) from wastewater samples

Magda A. Akl[a,1], Mohamed A. Hashem[a,1*], Aya G. Mostafa[a]

[a]Department of Chemistry, Faculty of Science, Mansoura University, Mansoura 35516, Egypt

Abstract

Semicarbazid modified flax fiber (SC.MFF) was successfully synthesized for the removal of Cr(IV) from different wastewater samples. Preparation of the SC.MFF material occurred in two main steps, the first step is the oxidation of the flax fibers by potassium periodate and the next step is refluxing of the oxidized fibers with semicarbazide ligand. The results show that quaternary ammonium cations were grafted on the surface of SC.MFF successfully. Additionally, a series of characterization of the SC.MFF sorbent was carried out using scanning electron microscopy, FTIR, elemental analysis, and X-ray diffraction spectroscopy. The effects of pH and ionic strength on the adsorption capacity were also investigated, which showed the adsorption capacity of the adsorbent decreased significantly with the increase of ionic strength and pH. Under optimized extraction conditions, the sorption capacity of Cr(VI) is 97.4 mg. g^{-1}. The kinetic studies show that the experimental data matches well with the pseudo-second-order kinetic model. Furthermore, the studied Cr(VI) adsorbed on the sorbent according to the Langmuir adsorption model. Finally, the SC.MFF sorbent was successfully applied for the selective and high-efficiency recovery of Cr(VI) ions from different water samples.

Keywords:
Modified flax fiber
Semicarbazid hydrochloride
Cationization
Cr(VI) ions

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* Corresponding author E-mail address: mohamed_chem28@yahoo.com (M. A. Hashem).

[1] These authors contributed equally to this work.

1. Introduction

There are two forms of chromium, trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). The hexavalent form is more toxic and carcinogenic than the trivalent. Cr(VI) is a highly accumulated ion in living organisms. Cr(III) has limited solubility in aqueous media and easy to precipitate. It is an essential element for human health at very low concentrations (between 50 to 200 mg/day). Chromium compounds are dangerous to human health as they harm the digestive system, skin, and respiratory system. Cr(VI) enters various industrial fields like metal finishing, electroplating, atomic power plants, and metallurgy. Its presence in the environment returns to many reasons such as improper storage, leakage, and disposal in water sources. Chromium discharge limits have been developed by some industrial countries to reduce environmental pollution. WHO organization has instituted the total chromium maximum to be 0.05 mg/L[1-5].

Several techniques are utilized in water treatment and metal separation like coagulation, membrane filtration, photocatalytic degradation, flotation, cloud point extraction, and adsorption [6-12]. Among them, adsorption has been considered a promising and effective treatment method. Simplicity, cheapness, ease of operation, and the recycling o the adsorbent are advantages of adsorption techniques. Its mechanism depends on Adsorbent-Adsorbate interactions[13-17]. Cellulose is a traditional low-cost efficient adsorbent, which has a high potential for heavy metal removal from wastewaters due to its abundance, chemical and mechanical stability, high adsorption capability, and unique structural properties

Cellulose has several advantages as it is cheap, renewable, available, regenerated, eco-friendly, and biodegradable. Also, it has a high uptake capacity and low density. Cellulose modifications occur to introduce functional groups. It is easily modified because of the presence of three hydroxyl groups in each cellulose unit. It is modified by several techniques like oxidation, esterification, etherification, and halogenation [18-27]. In recent years, ion-pair formation has been used to remove various organic and inorganic contaminants. The advantages of ion-pair formation include higher reactive surface area, faster and more complete reactions [28].

This study was motivated by these findings and took into account the synthesis of ion pairs between N-donor modified flax fiber and chromium ions to prepare an N-donor modified flax adsorbent for the removal of Cr(VI) via ion pair formation between N-donor modified flax fiber and chromium ions. For the functionalization with semicarbazone, flax fibers were oxidized with periodate before being condensed with Semicarbazide hydrochloride. The effects of many parameters that affect SC.MFF performance, such as pH, contact time, initial adsorption concentration, interfering ions, and reusability, were explored systemically. SC.MFF's applicability for the separation of Cr(VI) ions from various matrices was also assessed.

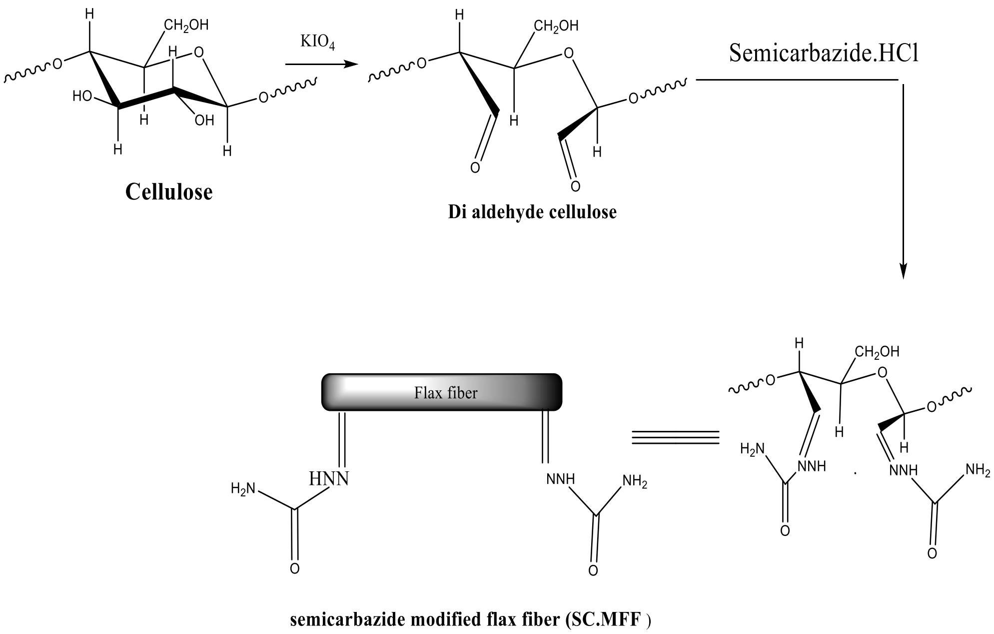
2. Experimental

2.1. Materials

Semicarbazide.HCl, potassium dichromate ($K_2Cr_2O_7$), and tri-ethylamine absolute ethanol, sodium hydroxide (NaOH), and hydrogen chloride (HCl), were purchased from Sigma Aldrich. All the purchased chemicals were used without any pre-treatment. Flax fibers were obtained from Tanta flax & oil company. Before use, flax fibers were washed by dist.H_2O and were dried in the oven at 50°C. potassium periodate 4% solution was prepared by dissolving 4 g of potassium periodate in 100 ml dist.H_2O. Semicarbazide.HCl 2% solution was prepared by adding 2 grams of semicarbazide.HCl in 100 ml absolute ethanol then, the mixture was heated until the semicarbazide.HCl dissolved in the ethanol.

2.2. Preparation of semicarbazide modified flax fiber (SC.MFF) sorbent

Flax fiber modified with semicarbazide (SC.MFF) was prepared in the following stepwise, scheme 1. At first, one gram of the native flax fiber was oxidized using 100 ml of 4% potassium periodate. The previous mixture was shaken for 1 hour in complete darkness to form dialdehyde cellulose. The obtained oxidized fiber was washed several times with dist.H_2O and was dried in the oven at 50°C. Then, one gram of oxidized flax fiber was refluxed with 100 ml of 2% alcoholic semicarbazide HCl and 0.5 ml tri-ethylamine for four hours at 70°C. Finally, the obtained modified fiber was washed several times with dist.H_2O. The modified flax fiber with Semicarbazide was dried in the oven at 50°C [29].



Scheme 1: Synthesis of SC.MFF adsorbent and adsorption of dichromate by SC.MFF.

2.3. Characterization of samples

A JSM-6510LV instrument was used to investigate morphological characterizations. Before analysis, all samples were sputter-coated by gold. IR spectra for the samples were recorded by using Fourier transform infrared spectrometer (Perkin–Elmer spectrum) (FT-IR). C, H, and N elemental analysis were measured by using Costech (ECS-4010) elemental analyzer (Costech, Italy). The remaining concentration of Cr(VI) has been measured using a Unicam UV 2100 UV/Visible spectrometer.

2.4. Dichromate ion adsorption and regeneration

The adsorption of Cr(VI) was carried out by batch experiments. Adsorption experiments were occurred out in 125 ml stopped bottles that were contained 50 ml of adsorbate solutions and adsorbent dose. Then the stoppered bottles were shaken at 150 rpm on the thermostated shaker at room temperature 25^{o}C. Sodium chloride was used to study the ionic strength parameter. Sodium hydroxide and hydrochloric acid were used to adjust the solution pH. Then the bottle contents were centrifuged after reaching the adsorption equilibrium. The liquid supernatant that contains the remaining un adsorbed Cr(VI) was measured. Various parameters were studied such as contact time (15-240 min), temperature parameter(25^{o}C-45^{o}C), adsorbent dose (0.025g-0.2g), pH parameter (2-8), adsorbate initial concentration (25-400mg/l), and ionic strength (0-0.2 mol/L).

Removal efficiency (%) and the amount of the adsorbed adsorbate at equilibrium q_e (mg/g) were determined using Eq1 and Eq2, respectively.

$$R = \frac{C_i - C_f}{C_i} \qquad \text{Eq1}$$

$$q_e = \frac{(C_i - C_f) * v}{wt} \qquad \text{Eq2}$$

Where, C_i (mg/L) is the initial adsorbate concentration, C_f (mg/L) is the equilibrium adsorbate concentration, wt (g) is the adsorbent dose, and V (L) is adsorbate solution volume.

Adsorbent material (SC.MFF) regeneration was carried out by adsorption-desorption experiments. At first, an adsorption batch experiment for Cr(VI) was carried out using 0.1 gram of SC.MFF and 50 ml 100ppm Cr(VI) solution at pH 2 and 25^{o}C for 3 hours. For desorption studies, K_2CO_3 0.1 M was used as an eluent. 50 ml of 0.1 M eluent and 0.1 g. of Cr-adsorbed SC.MFF was shaken for 1 hour. Finally, the regenerated adsorbents were used for another four repeated adsorption-desorption cycles.

2.5. Preparation of real samples

In 1000 ml of water, 0.5 g of potassium persulphate, $K_2S_2O_8$, and 5 ml of 98 percent (w/w) H_2SO_4 were added to elaborate the digestion of the wastewater samples. sample and heated for 2 h at 95^{o}C to digest all organic matter which may be present. After cooling to room temperature, 0.1 g of modified fiber was added to the sample and the pH value was adjusted to 2 with continuous stirring for 180 min, filter and again another 0.1 g of modified flax fiber was added to the filtrate to ensure the complete separation of analytes. The remaining Cr(VI) was determined by using Unicam UV 2100 UV/Visible spectrometer.

3. Results and discussion

3.1. Characterization

3.1.1 Infra-red spectra

FT-IR spectra were used to differentiate the several processes in the synthesis of SC.MFF as chelating fibers and the findings are presented in Figs 1a, b, and c. The IR spectra of native and oxidized flax fibers are shown in Figure 1. The native flax fiber IR spectra in fig.1.a showed peaks of C-O stretching vibrations at about 1070-1150 cm^{-1}, peaks of O-H bending vibrations at about 1250-1420 cm−1, and peaks of O-H stretching vibrations at about 3500-3200 cm^{-1}. The peak at about 1730 cm1 in the oxidized flax fibers IR spectra in fig.1.b could be due to aldehyde group stretching vibrations [30]. The spectra of the produced SC.MFF (Fig.1c) displays a new peak at almost 1680 cm-1 after the reaction with semicarbazide, which could be attributed to the azo-methane group of the Schiff base that formed between the dialdehyde groups of the oxidized flax fibers with semicarbazide.

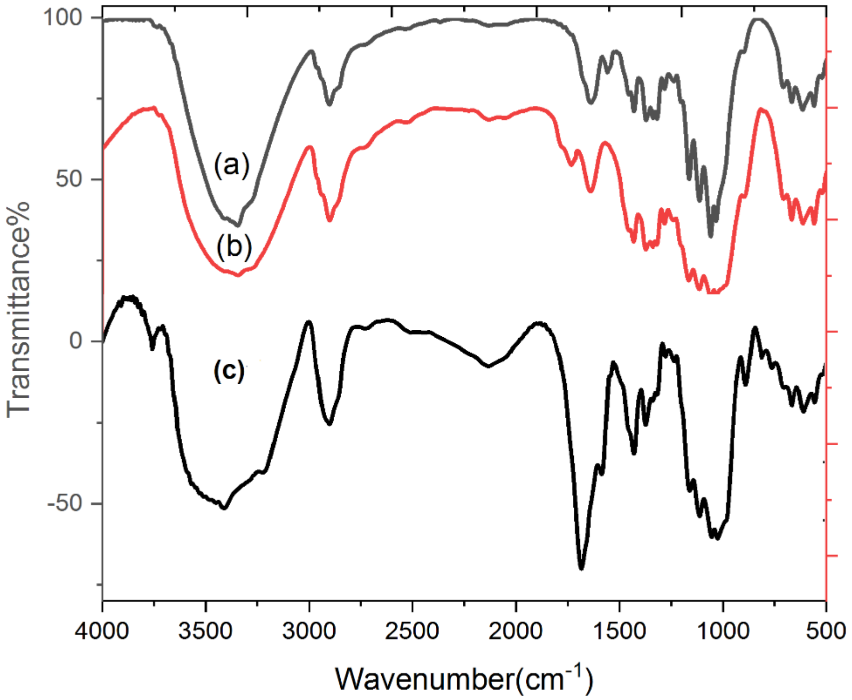


Fig.1: IR spectra of (a) native flax fiber and (b) oxidized flax fiber.(c) SC.MFF.

3.1.2 Elemental analysis

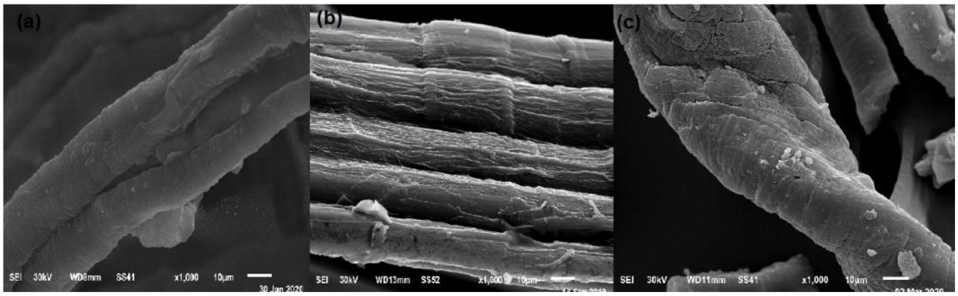
Table 1 shows the obtained elemental analysis results for both native flax and SC.MFF materials. Raising nitrogen percent from 0% in the case of native flax to 11.33% in the case of SC.HCl-MFF material is an indication for SC. MFF material formation. e insertedTh semicarbazide moieties were calculated to be approximately 1.41^{1-}mmol g .

Table1: elemental analysis of native and modified flax fibers.

fiber	C(%)	H(%)	N(%)
Native flax fiber	45	6.81	0
SC.MFF	34.36	5.08	11.33

3.1.3. Scanning electron microscope (SEM)

The surface morphology of native, oxidized, and modified flax fiber has been detected by the scanning electron microscope. The presence of narrow strips on the oxidized fiber surface is detected as present in fig.2. b and this may be returned to the periodate action during the oxidation process [31]. In fig.2.c, The surface becomes rougher than the native and oxidized surfaces, which could be owing to a chemical interaction between the semicarbazide molecules and the oxidized flax fiber to formation SC.MFF material.



(a) (b) (c)

Fig.2: SEM of (a) native flax fiber, (b) oxidized flax fiber, and (c) SCHCl.MFF.

3.*1.4. X-ray diffraction*

XRD patterns of native, oxidized, and modified flax fiber samples are shown in fig.3. The primary peak of crystalline flax at 22.835°, which corresponds to the (200) reflection, can be seen in the XRD patterns. Furthermore, the less intense peaks at 15.178o, 16.756°, and 34.475° correspond to (110), (110), and (004) reflections, respectively. The samples' crystallinity indices (CrI) were calculated using the Segal method.[32].

$$\mathrm{CrI\%} = \frac{I_{200} - I_{am}}{I_{200}} \text{ x } 100 \qquad \text{Eq. 3}$$

Where I_{200} is the maximum intensity of the crystal peak at 2 = 22.835° and I_{am} is the minimum intensity at 2 = 15.185°. The native, oxidized, and modified flax fibers have crystallinity indexes of 73.19, 71.77, and 71.24 percent, respectively. These results show that the ordered structure of crystalline flax fibers is unaffected by the modification procedure.

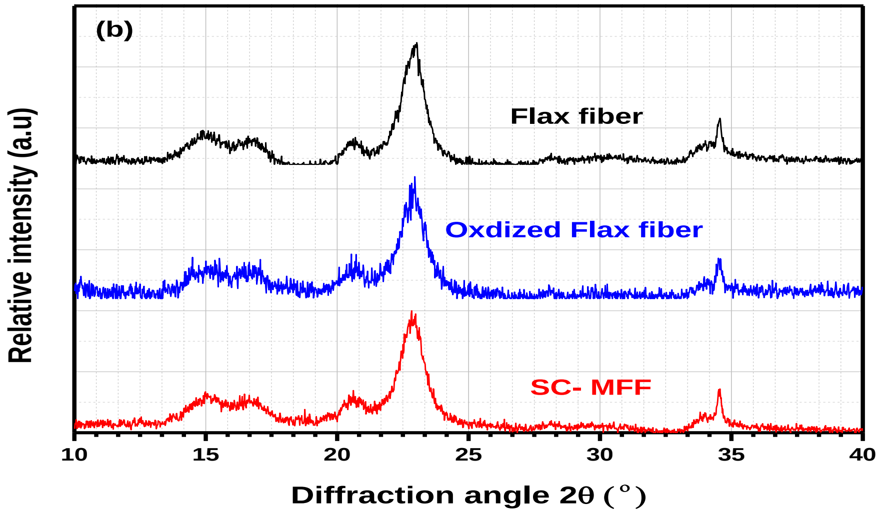


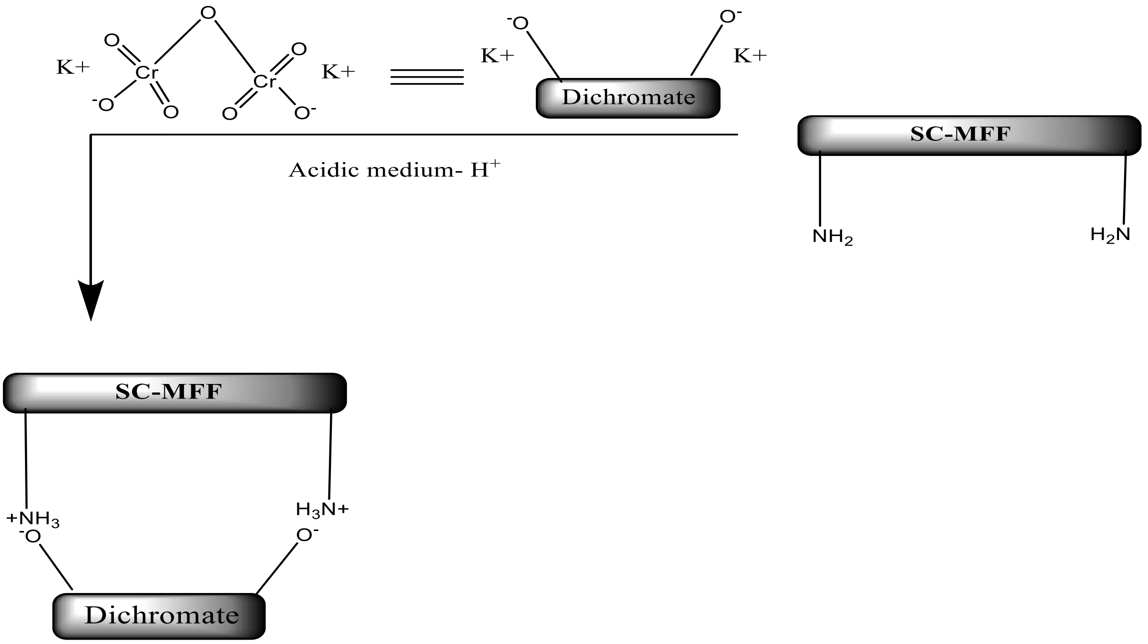
Figure 3. XRD patterns of flax, oxidized flax, and SC.MFF samples.

3.1.5. N_2 physisorption studies

The specific surface properties of the samples were evaluated using Brunauer-Emmett-Teller (BET) surface area analysis and Barrett-Joyner-Halenda (BJH) pore size and volume analysis. The Native flax fibers have a greater surface area (44.2151 m^2 g^{-1}) than the SC.MFF sorbent (10.3251 m2 g1), according to the specific surface area calculations. The decrease in specific surface area after chemical modification could be related to the anchoring of semicarbazide moieties in flax fiber pores, which inhibited the adsorption of N_2 molecules utilized in the surface area measuring technique. The functionalized fibers' limited surface area revealed that the adsorption process is primarily mediated by semicarbazone coordination.

3.1.6. Mechanism of sorption of dichromate ions onto SC-MFF

The surface charge of the raw flax fibers and SC. MFF was studied by zeta potential measurement in pH range 2–8, the isoelectric point of the flax fiber is 6.8, it is positive at low pH due to the protonation of amino and imino groups of SC.MFF ($-NH_2 + H^+ \rightarrow NH_3^+$). Particularly, owing to the introduction of NH_2-SC.MFF onto flax fibers, zeta potential value of SC.MFF is always higher than that of raw flax fiber over the whole pH range. This occurrence demonstrates NH_2-SC.MFF's superior electrostatic adsorption ability as an adsorbent component in modified flax fibers. The zeta potentials diminish and become negative when the pH value rises, owing to the deprotonation of homologous groups in an alkaline environment.



Scheme 2: Mechanism of sorption of dichromate ions onto SC-MFF

3.2. Optimization studies

3.2.1. Effect of pH

The adsorption of Chromium Cr(VI) is strongly affected by pH. So, the studying of pH is very important. The impact of pH was studied by taking 0.1 g of SC.MFF to 50 ml of the 100 mg/l Cr(VI) aqueous solution at 25°C for 3 hours. In pH range (2-8), the Cr(VI) uptake was examined as a function of hydrogen ion concentration as present in fig. 4. It was observed that the maximum adsorption capacity was at pH 2. Experimental data confirms that the adsorption capacity for Cr(VI) is highly pH-dependent. It was also observed that the decreasing of adsorption capacity with pH increasing from 2 to 8.

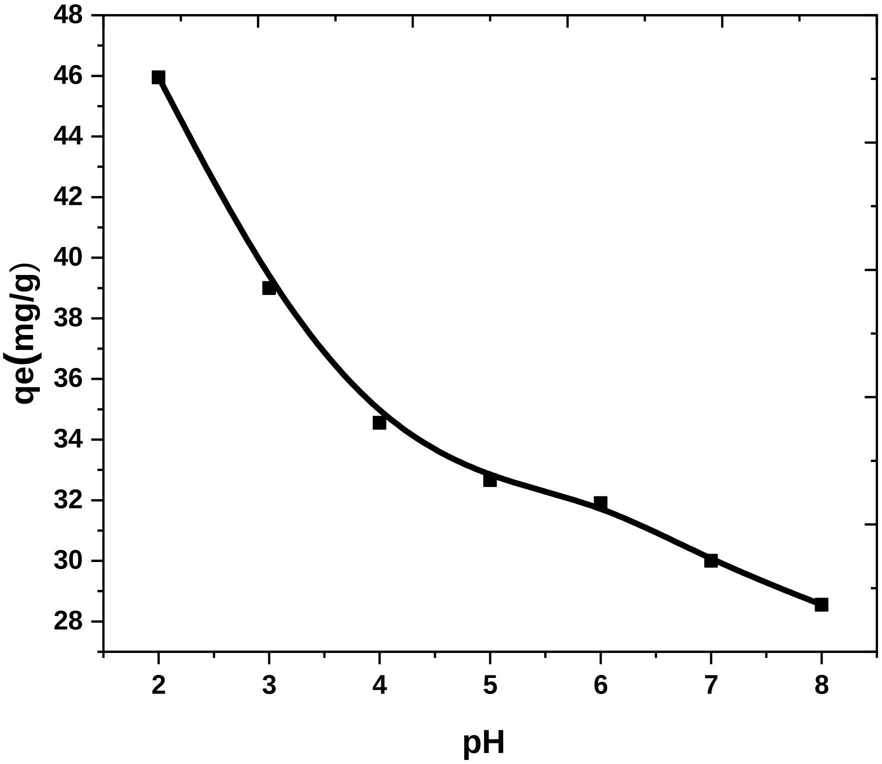


Fig. 4. Effect of pH on the recovery of 50 ml of 100 mg L^{-1} Cr(VI) ions by 0.1 g of SC.MFF sorbent at 25 °C after acontact time of 3h.

Cr(VI) anion in aqueous solutions may be present in many forms depending on pH. At pH between 2 and 6, both $Cr_2O_7^{2-}$ and $HCrO_4^-$ are present in equilibrium. $HCrO_4^-$ is the major species. With pH increasing $HCrO_4^-$ species converted into CrO_4^{2-} and $Cr_2O_7^{2-}$

species and at pH higher than 7.5 present in CrO_4^{2-} form only. Because of the strong protonation, the adsorbent surface becomes positively charged at low pH. The Cr(VI) adsorption was enhanced due to the electrostatic force between the negatively charged $HCrO^{-4}$ and $Cr_2O_7^{-2}$ and the positively charged adsorbent surface.

3.2.2. Effect of sorbent dose

Adsorbent dose parameter is very important in adsorption capacity determination. It was investigated by adding various weights of (SC.MFF) adsorbent in a 50 ml aqueous solution of 100 mg/L Cr(VI) at 25 °C for 3 hours. It was observed that the efficiency of the Cr(VI) removal increased from 62.5% to 91.9% with the adsorbent dose increasing from 0.025 g to 0.1 g and with adsorbent dose increasing from 0.1 g to 0.2 g, the removal efficiency showed few changes as present in fig. 4. This may be due to the adsorbent specific surface area increasing and the presence of more available adsorption sites. It is also observed that the decreasing of adsorption capacity from 125 mg/g to 23.16 mg/g with increase the dose from 0.025g to 0.2 g. The adsorbent dose of 0.1 gram was a sufficient dose for Cr(VI) removal.

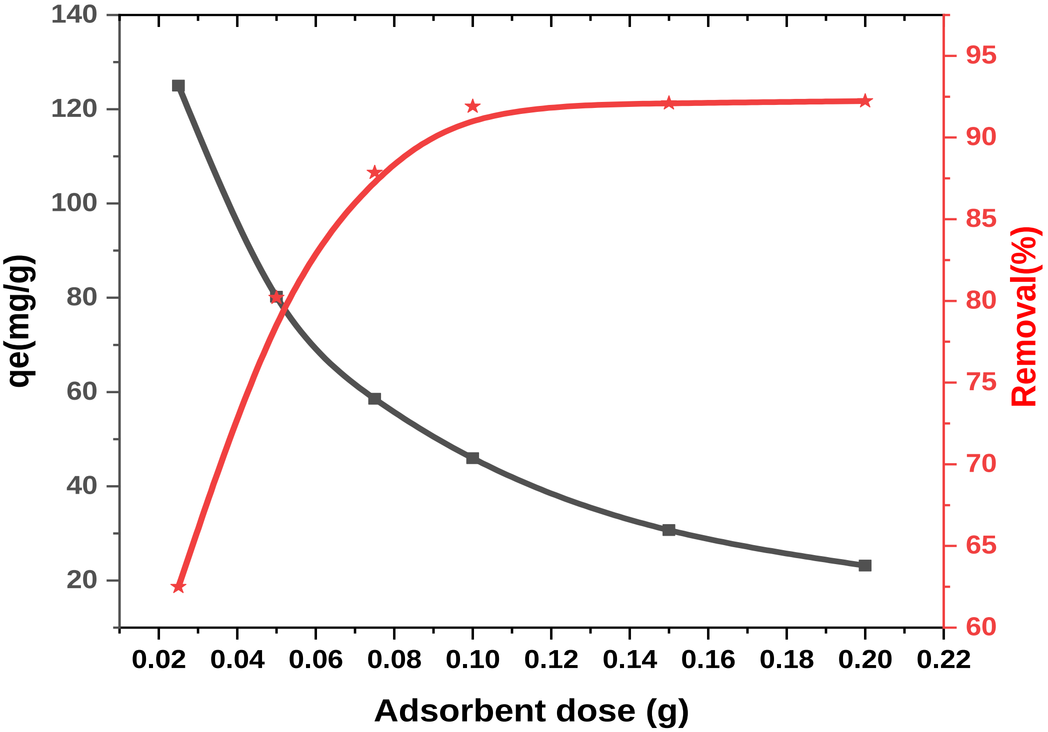


Fig. 5. Effect of adsorbent dose on adsorption of Cr(VI) onto (SC.MFF) adsorbent.

3.2.3. Effect of ionic strength on the adsorption capacity

Ionic strength parameter was studied by using Cl^- inorganic electrolyte in the form KCl. It was investigated by the addition of 0.1 g of SC.MFF

respectively to 50 ml aqueous solution of 100 mg/L Cr(VI) at 25°C for 3 hours and KCl concentration range between 0 mol/L and 0.2 mol/L. From experimental data that present in fig. 5 it was observed that with increasing inorganic electrolyte concentration, the adsorption capacity was decreased which confirmed that inorganic electrolyte presences suppress the Cr(VI) adsorption [4].

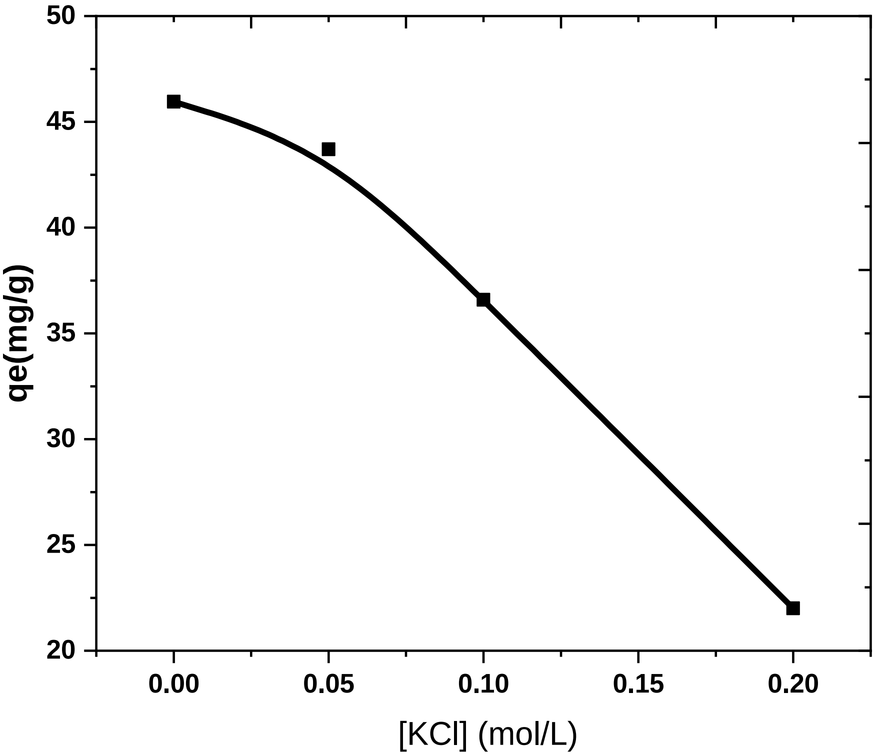


Fig. 6. Effect of ionic strength on adsorption capacity

3.2.4. *Adsorption kinetics*

Contact time is an important parameter for the investigation of sorption efficiency. The contact time parameter was studied at different adsorption times from 60 to 240 min by using 0.1 g of (SC.MFF) material as adsorbent doses that were respectively added to a series of bottles that contain 50 ml of 100 mg/l Cr(VI) solutions at 25°C as shown in fig.6.

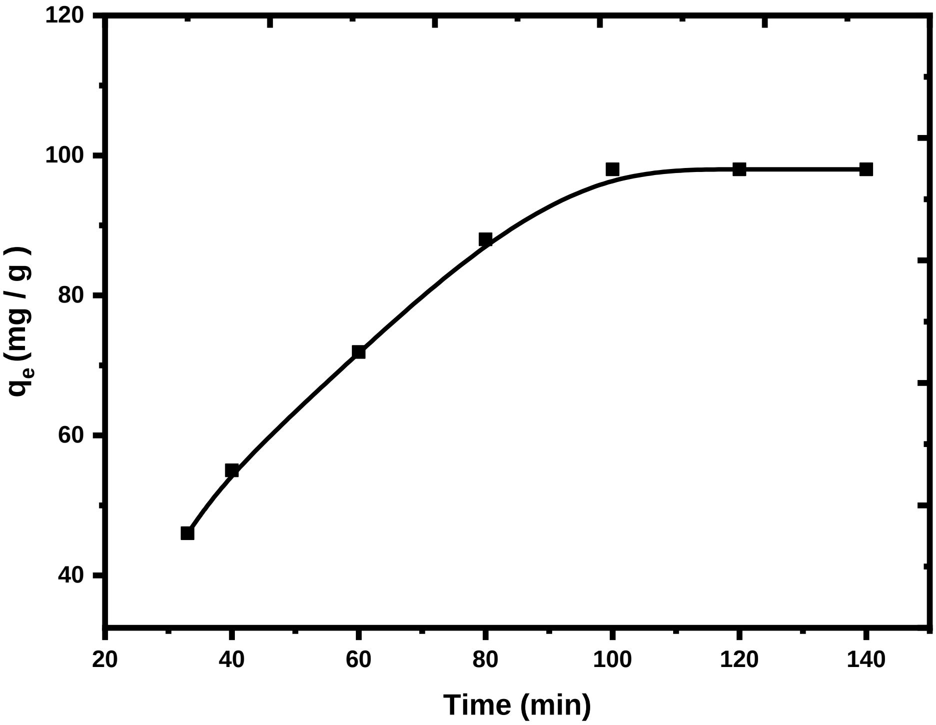


Fig.7: Influence of contact time on adsorption of Cr(VI) 50 ml of 100 mg.L^{-1} by SC.MFF sorbent (0.1 g), pH 2.0, rate of shaking 150 rpm, at 25°C.

The study of kinetic characteristics is crucial for designing the sorption system, better understanding the sorption mechanism, and identifying the adsorption rate-controlling step.

SC.MFF may exhibit a variety of interactions as a result of the presence of numerous active functional groups. The first type, as illustrated in Eq. 1, is a pseudo-first-order equation (4)

$1/q_t(\mathrm{ads}) = k_1/q_{e(\mathrm{ads})}t + 1/q_{e(\mathrm{ads})}$ Eq.(4)

and the pseudo-second-order equation as shown in Eq. (5)

$t/q_{t(\mathrm{ads})}=1/k_2q_e{}^2{}_{(\mathrm{ads})}+ (1/q_{e(\mathrm{ads})})t$ Eq.(5)

where qe(ads) (mg.g-1) and qt(ads) (mg.g-1) are the equilibrium and time t (min) adsorption abilities, respectively. The pseudo-second-order sorption rate constant is K_2, while the pseudo-first-order sorption rate constant is K_1. K and qe(ads) were commonly calculated jointly for the two models, and the one that came closest to the experimental adsorption data, as well as the correlation coefficient, were used to evaluate the kinetic model that matched the experimental work.vThe kinetic parameters for the current models are shown in Table (2). The experimental values, qe(ads), match the calculated values using pseudo-sequence analysis. correlation coefficients (R^2). Thus, the pseudo-second-order equation is suitable for the experimental kinetic data.

Table 2: Kinetic parameters for the adsorption of Cr(VI) by SC.MFF**.**

Fibers	First-order model		
	k_1 (min^{-1})	q_{e1ads}(mg/g)	R^2
Cr(VI) .SC-MFF	4.2	85.5±3	0.916
Fibers	**Second-order model**		
	k_2 (g/(mg min))	q_{e2ads} (mg/g)	R^2
Cr(VI) .SC-MFF	3.9×10^{-3}	97± 2	0.989

3.2.5. Effect of initial concentration on the adsorption capacity

The sorption isotherm studies, as shown in fig.8, are critical in explaining the nature of the interaction of Cr(VI) metal ions with chelating fibers.The Freundlich and Langmuir isotherm models were investigated.The results of the experiment were calculated and presented in table (3). The Langmuir model is the most well-fitted model with the generated experimental data based on the correlation coefficient values. The $Cr_2O_7^{--}$ maximum sorption capacity is 97.4mg/g.

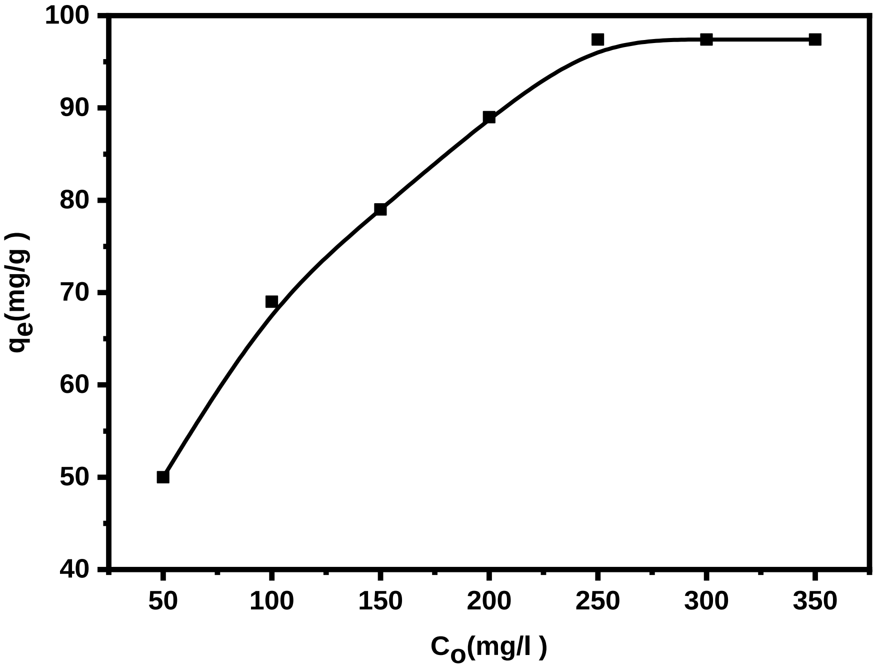


Fig.8: (a) Effect of initial concentration of Cr(VI) on adsorption capacity.

Table 3: Physicochemical adsorption of Cr(VI) metal ions by (SC.MFF) chelating fibers.

Fiber	**Langmuir isotherm constants**		
Cr(VI) . SC.MFF	**K_L(L/g)**	**q_m(mg/g)**	**R^2**
	0.05846	97.4	0.996
Fiber	**Freundlich isotherm constants**		
Cr(VI) . SC. MFF	**K_F**	**n**	**R^2**
	12.452	22.237	0.892

3.2.6. Effect of Temperature on the adsorption capacity

The adsorption of Cr(VI) was studied at different temperatures from 25 to 45˚C at pH 2 for 3 hours. Free energy parameter ($\Delta G^{o}ads$), adsorption entropy parameter (ΔS°ads), and heat of enthalpy parameter ($\Delta H^{\circ}ads$) of Cr(VI) metal ion adsorption by SC.MFF adsorbent were calculated. $\Delta G^{o}ads$ parameter was calculated from the following equations Eq6, Eq7, and Eq8.

$$K_C = C_{ad} / C_e \qquad \text{Eq.6}$$

$$\Delta G^{o}_{ads}n = -RT \ln K_C \qquad \text{Eq.7}$$

$$\ln K_C = \Delta S^{o}_{adsn} / R - \Delta H^{o}_{adsn} / RT \qquad \text{Eq.8}$$

where K_c is a thermodynamic equilibrium constant, C_{ad} is the Cr(VI) concentration taken by SC.HCl-MFF material at equilibrium (mg/g), C_e is the Cr(VI) concentration at equilibrium (mg/L), and R is the universal gas constant.

The rest of the parameters (ΔH^{o}_{adsn} and ΔS^{o}_{adsn}) were calculated from the plot of ln K_c vs. 1/T as the slope of the plotting equals ($-\Delta H^{o}_{adsn}$ /R), and the intercept equals (ΔS^{o}_{adsn} /R).

From the experimental data present in table 4, it was noticed that the negative ΔG^{o}adsn value confirms that the Cr(VI) adsorption by SC.MFF material is a spontaneous process. It was also observed that the negative ΔH^{o}ads value confirms that the Cr(VI) adsorption by SC.MFF material is exothermic. The negative ΔS^{o}ads value showed that Cr(VI) metal ion adsorption onto SCMFF surface leads to lower disorder and higher arrangement.[29-32]

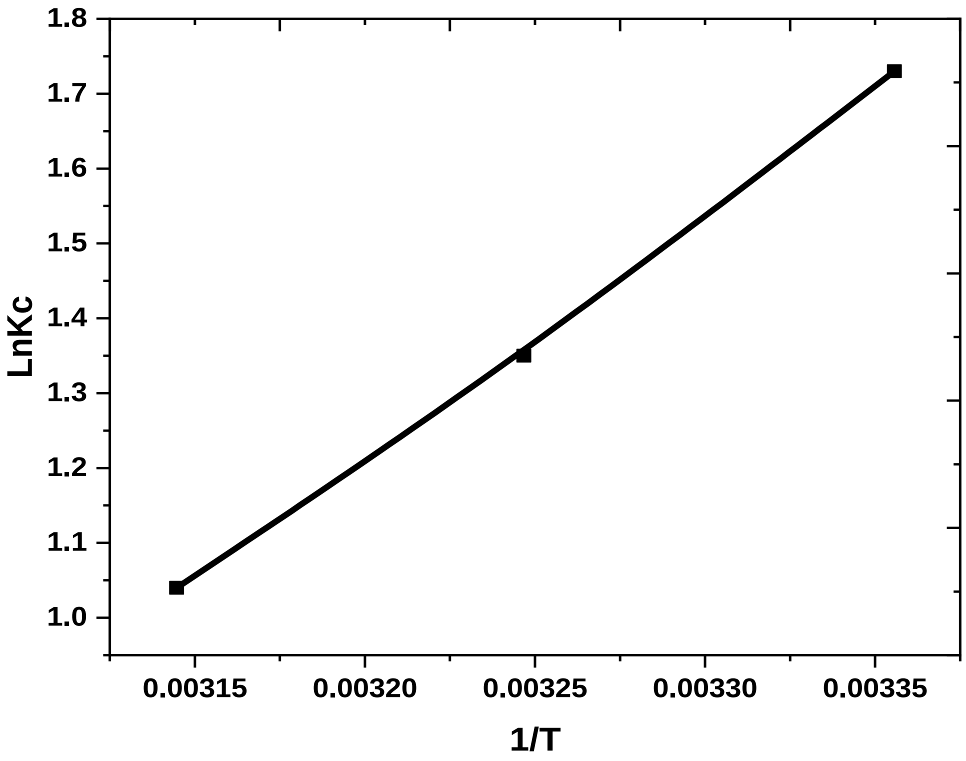


Fig.9: Plot of ln K_C as a purpose of (1/T) absolute temperature for the adsorption of single metal cations Cr(VI).

Table 4: Thermodynamic parameters for the adsorption of single metal ions Cr(VI) on SC.MFF

System	T (k)	Kc	ΔGoads (KJ/mol)	ΔH^o_{ads} (KJ/mol)	ΔS^o_{ads} (J/mol K)
Cr(VI).SC.MFF	298	5.672	4.286	-27.2	-76.96
	308	3.857	3.4569		
	318	2.85	2.7496		

3.2.7. *Desorption and reusability studies*

Five adsorption-desorption cycles were done under ideal conditions to assess the SC.MFF reusability.The desorption of the target metal ions from the SC.MFF polymer was examined using varied volumes of 0.1 mol L-1 K_2CO_3 as an eluting agent. From the data presented in table 4, it has been observed that the SC.MFF has high sorption efficiency after five cycles (higher than 92%). So, it is predictable that SC.MFF could be a good sorbent for Cr(VI) removal from the dist.H_2O.

Table 4: Repeated adsorption of metal ions Cr(VI) (50 ml of 50 mg L^{-1}) by SC.MFF sorbent (0.10 g), pH 2, time of shaking 60 min, 25°C, desorption by 5 mL of 0.1 mol L^{-1} K_2CO_3.

Cycle number	Recovery (%)
1	98.9
2	97.3
3	94.8
4	93.6
5	92.0

3.2.8. Application on real samples

Spiked wastewater samples were used to evaluate the removal efficiency of the new sorbent SC.MFF. From the experimental results in Table 5, it is noticed that a good covenant was achieved between the added metal ion concentration and the obtained one by using the test procedure. The recoveries higher than 90% show that the anticipated procedure gives a suitable accuracy on spiked samples analysis.

Table 5. Analysis of spiked samples by new sorbent SC.MFF

Wastewater samples locations	Metal ions	Added (µg mL^{-1})	Found (µg mL^{-1})	Recovery (%)	RSD (%)
Mansoura	Cr(VI)	150	136.38	90.08	1.22
Sinbellawin		150	136.05	93.01	1.30
Mokataa		150	135.87	94.22	1.23
Talkha		150	135.72	95.23	1.24
Manzalla		150	135.56	96.32	1.29

3.2.9. Comparison of the proposed adsorbent with other cited adsorbents

The proposed adsorbent can recover and separate Cr(VI) ions with high precision and extraction efficiency from a variety of matrices. Table 6 compares the performance of the current adsorbent to that of other adsorbents previously described in the literature. The sorption capacity and kind of sample matrices on which the separation is performed should be taken into account while evaluating various adsorbents for SC.MFF separation. In comparison to other adsorbents, as indicated in Table (6), the current adsorbent has comparatively high capacities for the recovery of Cr(VI) ions.

Table 6: Comparison of equilibrium time of various adsorbents for Cr(VI).

Adsorbent	Adsorbent dose	Cr(VI) initial concentration (ppm)	Sorption capacity (mg/g)	Reference
pineapple peel derived biochars	5g/l	10	41.67	[33]
sugarcane bagasse magnetic biochar	0.1g/25ml	100	43.122	[34]
Fe3O4 @ Cr(VI) IIPs	80 mg/10 ml	12	2.49	[35]
Fe3O4 @ Cr(VI) NIPs	80 mg/ 10ml	12	0.52	[35]
Cellulose-1N	6.1 mg/ 20ml	50	10.2	[36]
Cellulose-2N	6.1 mg/ 20ml	50	18.1	[36]
Cellulose-3N	6.1 mg/ 20ml	50	34.7	[36]
Semicarbazide.HCl modified flax fiber	0.1g/ 50ml	100 ppm	97.4	Present study

4. Conclusion

This research includes the preparation, characterization, usage as an adsorbent, regeneration, and application of Semicarbazide modified flax fiber(SC.MFF). Preparation of the SC.MFF material occurred in two main steps, the first step is the oxidation of the flax fibers by potassium periodate and the next step is Refluxing of the oxidized fibers with semicarbazide ligand. The prepared material characterizations were explored by using various techniques like infra-red spectroscopy (FTIR), elemental analysis (EA), and scanning electron microscope (SEM). SC.MFF adsorbent was used for removing hexavalent chromium from an aqueous solution. Some parameters were studied to evaluate the optimum conditions like contact time, adsorbent dose, pH, ionic strength, metal ion initial concentration, and temperature. Isothermal models (Langmuir and Freundlich) were studied. The prepared material was regenerated using K_2CO_3. It was applied for the removal of the hexavalent chromium from real wastewater samples.

References

[1] N. S. Neki, A. Singh, G. S. Shergill, and A. Kaur, “ACUTE POTASSIUM DICHROMATE POISONING : AN OVERVIEW,” vol. 21, no. December, pp. 1–7, 2016.

[2] H. Wang *et al.*, “Facile synthesis of heterojunction of MXenes / TiO 2 nanoparticles towards enhanced hexavalent chromium,” *J. Colloid Interface Sci.*, 2019.

[3] V. Sureshkumar and S. C. G. K. Daniel, “Fabrication of chitosan – magnetite nanocomposite strip for chromium removal,” 2015.

[4] W. Jinhua *et al.*, “Rapid adsorption of Cr (VI) on modified halloysite nanotubes,” *Desalination*, vol. 259, no. 1–3, pp. 22–28, 2010.

[5] D. N. Swami and S. K. Gupta, “Adsorption Kinetics for the Removal of Chromium (VI) from Synthetic Waste Water Using Adsorbent Derived from Saw Dust, Bark and Rice Husk,” no. Vi, pp. 153–163, 2002.

[6] M. A. Akl, “Removal of Iron and Manganese in Water Samples Using Activated Carbon Derived from Local Agro-Residues,” *J. Chem. Eng. Process Technol.*, vol. 04, no. 04, 2013.

[7] M. Bagtash, “Hybrid central composite design for simultaneous optimization of removal of methylene blue and alizarin red S from aqueous solutions using Vitis tree leaves,” no. June, pp. 1–13, 2017.

[8] J. Zolgharnein, Z. Choghaei, M. Bagtash, S. Feshki, and M. Rastgordani, “Nano-Fe 3 O 4 and corn cover composite for removal of Alizarin Red S from aqueous solution : characterization and optimization investigations,” vol. 3994, no. May, 2016.

[9] P. Nuengmatcha, R. Mahachai, and S. Chanthai, “Adsorption Capacity of the as-Synthetic Graphene Oxide for the Removal of Alizarin Red S Dye from Aqueous Solution,” 2016.

[10] Magdi E. KHALIFA, Ibrahim M. M. KENAWY, Mohamed M. HASSANIEN, Mohamed M. ELNAGAR, Mixed Micelle-mediated Extraction and Separation of Scandium from Yttrium and Some Lanthanide Ions. Analytical Sciences 32(2016) 395-400

[11] Mohamed M.Hassanien, Ibrahim M.M.Kenawy, Magdi E.Khalifa, Mohamed M.Elnagar, Mixed micelle-mediated extraction approach for matrix elimination and separation of some rare earth elements. Microchemical Journal. 127 (2016) 125-132

[12] Mohamed M.Elnagar, Mohamed A.Hashem, Mohamed M.Hassanien, Mohamed A.Ismail, pH-controlled mixed micelle cloud point extraction for selective removal of trace levels of iron from titanium concentrates. Separation and Purification Technology. 265(2021) 118534

[13] E. A. Deliyanni, G. Z. Kyzas, and K. A. Matis, “Various flotation techniques for metal ions removal,” *J. Mol. Liq.*, vol. 225, pp. 260–264, 2017.

[14] M. Taseidifar, F. Makavipour, R. M. Pashley, and A. F. M. M. Rahman, “Removal of heavy metal ions from water using ion flotation,” *Environ. Technol. Innov.*, vol. 8, pp. 182–190, 2017.

[15] M. Bilal *et al.*, “Application of conventional and modified cloud point extraction for simultaneous enrichment of cadmium, lead and copper in lake water and fish muscles,” *J. Ind. Eng. Chem.*, vol. 40, pp. 137–144, 2016.

[16] A. MA and M. MM, “Enhanced Removal of Some Cationic Dyes from Environmental Samples Using Sulphuric Acid Modified Pistachio Shells Derived Activated Carbon,” *J. Chromatogr. Sep. Tech.*, vol. 7, no. 4, 2016.

[17] A. I. Abd-Elhamid, G. F. El Fawal, and M. A. Akl, "Methylene blue and crystal violet dyes removal (as a binary system) from aqueous solution using local soil clay: Kinetics study and equilibrium isotherms," *Egypt. J. Chem.*, vol. 62, no. 3, pp. 941–954, 2019.

[18] S. Hokkanen, A. Bhatnagar, and M. Sillanpää, "A review on modification methods to cellulose-based adsorbents to improve adsorption capacity," *Water Res.*, vol. 91, pp. 156–173, 2016.

[19] Y. Li, H. Xiao, Y. Pan, and L. Wang, "Novel Composite Adsorbent Consisting of Dissolved Cellulose Fiber/Microfibrillated Cellulose for Dye Removal from Aqueous Solution," *ACS Sustain. Chem. Eng.*, vol. 6, no. 5, pp. 6994–7002, 2018.

[20] X. Yue, J. Huang, F. Jiang, H. Lin, and Y. Chen, "Synthesis and characterization of cellulose-based adsorbent for removal of anionic and cationic dyes," *J. Eng. Fiber. Fabr.*, vol. 14, 2019.

[21] V. Bisla, G. Rattan, S. Singhal, and A. Kaushik, "Green and novel adsorbent from rice straw extracted cellulose for efficient adsorption of Hg (II) ions in an aqueous medium," *Int. J. Biol. Macromol.*, vol. 161, pp. 194–203, 2020.

[22] R. Kumar and R. K. Sharma, "Synthesis and characterization of cellulose based adsorbents for removal of Ni(II), Cu(II) and Pb(II) ions from aqueous solutions," *React. Funct. Polym.*, vol. 140, no. April, pp. 82–92, 2019.

[23] Y. Wang *et al.*, "Kinetic, isotherm, and thermodynamic studies of the adsorption of dyes from aqueous solution by cellulose-based adsorbents," *Water Sci. Technol.*, vol. 77, no. 11, pp. 2699–2708, 2018.

[24] X. Liang *et al.*, "A cellulose-based adsorbent with pendant groups of quaternary ammonium and amino for enhanced capture of aqueous Cr(VI)," *Int. J. Biol. Macromol.*, vol. 148, pp. 802–810, 2020.

[25] N. Sun, X. Wen, and C. Yan, "Adsorption of mercury ions from wastewater aqueous solution by amide functionalized cellulose from sugarcane bagasse," *Int. J. Biol. Macromol.*, vol. 108, pp. 1199–1206, 2018.

[26] H. Zhou, H. Zhu, F. Xue, H. He, and S. Wang, "Cellulose-based amphoteric adsorbent for the complete removal of low-level heavy metal ions via a specialization and cooperation mechanism," *Chem. Eng. J.*, vol. 385, no. December 2019, p. 123879, 2020.

[27] F. Xue, H. He, H. Zhu, H. Huang, Q. Wu, and S. Wang, "Structural Design of a Cellulose-Based Solid Amine Adsorbent for the Complete Removal and Colorimetric Detection of Cr(VI)," *Langmuir*, vol. 35, no. 39, pp. 12636–12646, 2019.

[28] Liu, Y., Phenrat, T., Lowry, G.V., 2007. Effect of TCE concentrationand dissolved groundwater solutes on NZVI-promoted TCEdechlorination and H2evolution. Environ. Sci. Technol. 41,7881e7887.

[29] M. A. Hashem, M. M. Elnagar, I. M. Kenawy, and M. A. Ismail, "Synthesis and application of hydrazono-imidazoline modified cellulose for selective separation of precious metals from geological samples," *Carbohydr. Polym.*, vol. 237, no. March, p. 116177, 2020.

[30] M. Monier, I. M. Kenawy, and M. A. Hashem, "Synthesis and characterization of selective thiourea modified Hg(II) ion-imprinted cellulosic cotton fibers," *Carbohydr. Polym.*, vol. 106, no. 1, pp. 49–59, 2014.

[31] I. M. Kenawy, M. A. H. Hafez, M. A. Ismail, and M. A. Hashem, "Adsorption of Cu(II), Cd(II), Hg(II), Pb(II) and Zn(II) from aqueous single metal solutions by guanyl-modified cellulose," *Int. J. Biol. Macromol.*, vol. 107, pp. 1538–1549, 2018.

[32] Segal, L., Creely, J.J., Martin Jr., A.E. and Conrad, C.M. (1959) An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using the X-Ray Diffractometer. Textile Research Journal, 29, 786-794.

[33] A. M. Yusof and N. A. N. N. Malek, “Removal of Cr(VI) and As(V) from aqueous solutions by HDTMA-modified zeolite Y,” *J. Hazard. Mater.*, vol. 162, no. 2–3, pp. 1019–1024, 2009.

[34] U. S. Army, “Removal of hexavalent chromium from gro...pdf,” vol. 37, no. Gadd 2010, pp. 102–126, 2013.

[35] L. Dupont and E. Guillon, “Removal of hexavalent chromium with a lignocellulosic substrate extracted from wheat bran,” *Environ. Sci. Technol.*, vol. 37, no. 18, pp. 4235–4241, 2003.

[36] X. Qi, S. Gao, G. Ding, A.N. Tang, Synthesis of surface Cr (VI)-imprinted magnetic nanoparticles for selective dispersive solid-phase extraction and determination of Cr (VI) in water samples, Talanta. 162 (2017) 345–353.