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Removal of Cr(VI) and Toxic Ions from Aqueous Solutions and Tannery Wastewater Using Polymer-Clay Composites

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Abstract: Polymer-clay composites were prepared by natural zeolite (clinoptilolite) or naturally local clay deposits in an *N,N*-methylene-bis-acrylamide as cross-linked. The resultant composites were used for the removal of Cr(VI) from an aqueous solution. Additionally, their effects on soluble ions of tannery wastewater were investigated. The produced composites were characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM). The results showed that Cr(VI) removal is dependent upon initial concentrations and pH. The adsorption quantity of Cr(VI) onto the polymerized clay deposit followed by polymerized zeolite exhibited higher values than their original samples. The polymer-clay composite of clay deposit showed the highest removal of 76.3–100% overall initial concentrations of 10–50 mg L^{−1} and at initial pH of 2. Kinetics of Cr(VI) removal by various sorbents was predicted using a pseudo-second order model. Our findings showed that the levels of salinity and various soluble ions (Cr²⁺, Na⁺, Cl[−] and SO₄^{2−}) in tannery wastewater are very high, and their levels were reduced after treatment, especially by polymerized sorbents. It could be concluded that the polymer-clay composites may be employed as a highly efficient sorbent for the removal of Cr(VI) and toxic ions from the wastewater.

Keywords: zeolite; clay deposit; composites; polymerization; chromium; sorbent

1. Introduction

The leather industry is considered one of the industries that contributes most to environmental pollution [1,2]. Tannery wastewater contains large amounts of pollutants including sodium chloride, sodium sulfate, toxic metallic compounds of chromium, and various other organic and inorganic compounds [1–4]. The tanning industries discharge their effluents into nearby lands or rivers, damaging the environmental compartments and thus causing serious harm to human health [2,4,5].

The removal of salts and toxic metallic compounds such as chromium ions from tannery liquid waste is a necessary action to protect public health and the environment. In this context, several traditional techniques for the removal of contaminants from wastewater and effluents were conducted using different means, including chemical precipitation, oxidation and reduction, ion exchange, electrochemical treatments, and reverse osmosis [6–11]. However, these techniques are mostly characterized by their high cost and difficulty. Recently, the use of clay minerals and their modified forms, such as a high specific surface area and high cation exchange capacity (CEC) with chemical and mechanical stability, has received much attention as an effective sorbent [12,13]. Among aluminosilicate

minerals, zeolite is considered to be a highly efficient sorbent for the removal of heavy metals from wastewater [14]. Zeolite and other aluminosilicate minerals have the ability to remove cationic metals due to their permanent negative charges [15]. However, the use of zeolite and aluminosilicate minerals may not be effective for removing negatively charged ions such as negatively charged species of Cr(VI) from wastewater. In addition, applying clay minerals in wastewater purification may make water flow difficult. Blends containing polymers have been reported to be a more economical technique for synthesizing new materials with novel characteristics for various uses [16–19]. Additionally, polymeric materials can show strong mechanical properties, good thermal stability, chemical neutrality, good adsorption characteristics, and easy regeneration [16–18]. In the literature, the interaction of polymer with minerals surfaces has been well documented [20]. It has been reported that the retention of polymer onto the mineral surfaces can occur through physical entrapment and chemical adsorption [20]. The modification of clay minerals using polymers results in the improved physical and chemical characteristics of surface clay mineral-polymer composites, which are of importance in producing composite materials, catalysts, and adsorbents [20]. The polymerization of clay minerals to form composites has been also reported to enhance clay efficiency for pollutants removal through its functional groups linked to clay particles [21]. Additionally, the linked polymer-to-clay particles can also prevent their coagulation in aqueous media. Several studies have shown that enhancing the adsorption capacity of various materials to remove negatively charged ions can be achieved by polymerization process [22,23]. Previous researchers have also shown that polymer composites are suited for both organic and inorganic contaminants in water through complexation [13].

Therefore, this study aimed to (1) synthesis polymer-clay composites by natural zeolite (clinoptilolite) or naturally occurring local clay deposits in a *N,N*-methylene-bis-acrylamide as cross-linked, (2) investigate the resultant composites for the Cr(VI) ions removal from aqueous solution, and (3) investigate the resultant composites for desalinizing and removal of some toxic ions (Cr, Na, Cl, and SO_4) from a real tannery wastewater.

2. Materials and Methods

2.1. Sample Collection, Preparation, and Synthesis

Naturally occurring deposits of aluminum silicate rich in zeolite were collected from Shama Mountain (20°44'29.1''N; 39°42'04.8''E), Saudi Arabia, while the natural zeolite used in this study was clinoptilolite (Morgan Co., Morgan, Mountain Green, UT, USA). The samples of natural zeolite and naturally occurring local clay deposits were washed with deionized water, allowed to air-dry, and then sieved using 50 μm .

The samples of natural zeolite and naturally occurring local clay deposits were grafted using polyacrylamide according to Shigetomi et al. [24]. Specifically, 25.0 g of each clay sample was put in 250 mL aqueous solution (2.5 g *N,N*-methylenebisacrylamide and 1.5 g potassium peroxydisulfate). Then, 7.5 g of acrylamide was added, the mixture was stirred at 70 °C. After that, the resultant polymerized materials were rinsed with deionized water and dried at 80 °C.

2.2. SEM, XRD, and FTIR Analysis

Scanning electron microscope (SEM; FEI, Inspect S50, The Netherlands) was employed to identify the morphological changes in the surface structure of raw and modified samples. X-ray diffraction (XRD) analysis (XRD-7000 Shimadzu, Japan) was used to identify any crystallographic structure in the adsorbents. Fourier transformation infrared analysis (Nicolet 6700 FT-IR, Thermo Fisher Scientific, Madison, WI, USA) of the adsorbent samples was performed in the wave number range of 400–4000 cm^{-1} in order to characterize their surface functional groups.

2.3. Adsorption Experiments

2.3.1. The Influence of Initial pH

The influence of initial feed pH of the aqueous solution on Cr(VI) adsorption onto various adsorbents was carried out using an aqueous solution (50 mL) containing $K_2Cr_2O_7$ (at concentration of 20 mg Cr(VI) L^{-1} adjusted at pH of 2, 4, 6, 8, and 10 using 0.1 M HCl and 0.1 M NaOH. The solutions were shaken for 120 min in plastic containers containing 0.5 g of each adsorbent. After that, suspensions were centrifuged, and the concentrations of Cr(VI) in the supernatant solutions were analyzed colorimetrically using a spectrophotometer following United State Environmental Protection Agency (USEPA) Method-7196A [25].

2.3.2. The Influence of Contact Time

To investigate the equilibrium dynamics, duplicate samples (0.5 g) of each sorbent were shaken for 5, 15, 30, 60, 80, and 120 min in polypropylene centrifuge tubes at room temperature with 50 mL of aqueous solution containing $K_2Cr_2O_7$ (at concentration of 20 mg Cr(VI) L^{-1} and initial pH of 2). Then, suspensions were centrifuged, and the concentrations of Cr(VI) in the supernatant solutions were analyzed colorimetrically by using a spectrophotometer. The following different kinetic models (Equations (1)–(4)) were applied to describe adsorption of Cr(VI) by using each sorbent [26].

$$\text{Pseudo-second order model: } t/q_t = 1/k_2q_e + 1/q_e t \quad (1)$$

$$\text{Elovich model: } q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t) \quad (2)$$

$$\text{Power function model: } \ln q_t = \ln b + k_f (\ln t) \quad (3)$$

$$\text{Intraparticle diffusion model: } q_t = a + k_{id} t^{1/2} \quad (4)$$

where: q_e and q_t are the amounts of Cr(VI) adsorbed at equilibrium and time t (min) in ($mg\ g^{-1}$), respectively, k_2 is the rate constant of second-order adsorption ($g\ mg^{-1}\ min^{-1}$), k_{id} is intraparticle diffusion rate ($mg\ g^{-1}\ min^{-0.5}$), k_f is rate coefficient value ($mg\ g^{-1}\ min^{-1}$), α is initial adsorption rate ($mg\ g^{-1}\ min^{-1}$), β is a constant ($mg\ g^{-1}$) $^{-1}$, and a and b are constants.

2.3.3. Adsorption Isotherm

An amount (0.5 g) of raw and polymerized adsorbents of natural zeolite and naturally occurring local clay deposits was weighed and put into 100 mL glass bottles. Duplicate samples (0.5 g) of each sorbent were shaken for 120 min in polypropylene centrifuge tubes at room temperature with 50 mL of the solution containing $K_2Cr_2O_7$ (at a concentration of 10–50 mg Cr(VI) L^{-1} and initial pH of 2). The quantities of Cr(VI) adsorbed by the various adsorbents were determined using the following equation (Equations (5)):

$$q_e = V(C_o - C_e)/m \quad (5)$$

where q_e is Cr(VI) concentration on the adsorbents ($mg\ g^{-1}$) at equilibrium, C_e is Cr(VI) concentration in solution ($mg\ L^{-1}$) at equilibrium, C_o is initial metal concentration in solution ($mg\ L^{-1}$), V is the used volume of initial aqueous solution (L), and m is mass of adsorbent (g).

Sorption isotherm parameters were obtained by applying the following models (Equations (6)–(8)) [27]:

$$\text{Langmuir model: } C_e/q_e = 1/(K_a q_m) + C_e/q_m \quad (6)$$

$$\text{Freundlich model } \log q_e = \log K_f + (1/n) \log C_e \quad (7)$$

$$\text{Temkin model: } q_e = a + b \ln C_e \quad (8)$$

where C_e = equilibrium concentration (mg L^{-1}) in solution phase, q_e = equilibrium concentration (mg g^{-1}) in solid phase, q_m = Maximum sorption capacity (mg g^{-1}), K_a = sorption constant (L mg^{-1}) in relation to enthalpy, n = sorption constant in relation to intensity, K_f = sorption capacity constant (L mg^{-1}), and a and b = constants in relation to adsorption energy and capacity.

2.4. Characterization of Tannery Wastewater and Its Treatment

The wastewater samples were collected from a number of tannery factories from Riyadh, Saudi Arabia. The collected samples were filtered and stored for the chemical analysis. The wastewater samples were analyzed for various chemical properties including pH, electrical conductivity (EC), soluble anions and cations and toxic heavy metals including Cr^{2+} , Cd^{2+} , and Pb^{2+} . The wastewater pH and EC were measured using a digital pH and EC meter, respectively. The concentrations of soluble Na^+ , SO_4^{2-} , and Cl^- were also measured using Ion Chromatography (IC; Dionex 5000, Sunnyvale, CA, USA). The toxic heavy metals (Cr^{2+} , Cd^{2+} , and Pb^{2+}) concentrations were analyzed using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES; Perkin Elmer Optima 4300 DV, Norwalk, CT, USA).

In this study, the influence of raw and modified sorbents through polymerization on the removal of soluble ions (Cr^{2+} , Na^+ , SO_4^{2-} , and Cl^-) from tannery wastewater was also investigated. The wastewater samples were shaken in plastic containers containing 1, 2, 4, 6, 8, and 10 g sorbent L^{-1} for 2 h. Then, for equilibrium, the mixtures were allowed to stand for 24 h. Concentrations of soluble Cr^{2+} in the supernatant solutions were analyzed after acidification using HNO_3 by ICP-OES. Additionally, soluble ions of Na^+ , SO_4^{2-} , and Cl^- at a sorbent dose of 10 g L^{-1} were analyzed using IC.

3. Results and Discussion

3.1. Characterization of the Raw and Polymer-Clay Composites

Powder X-ray diffraction patterns of natural zeolite or naturally occurring local clay deposits and their obtained composites (polymer-zeolite and polymer-clay deposit) are shown in Figure 1. The XRD spectra of the raw natural zeolite and clay deposit have different peaks. The XRD results indicate that raw natural zeolite is characterized by clinoptilolite as dominated mineral. The XRD spectra of raw clay deposit show the presence of the following minerals: chabazite (at 9.41, 3.93, and 2.12 Å), analcime (3.4, 5.6, and 2.69 Å), feldspar (at 4.02 and 3.19 Å) and quartz (at 3.34 Å). By comparing the XRD data of the polymer-samples with those of raw samples, some deviations in 2θ and d-spacing values were detected.

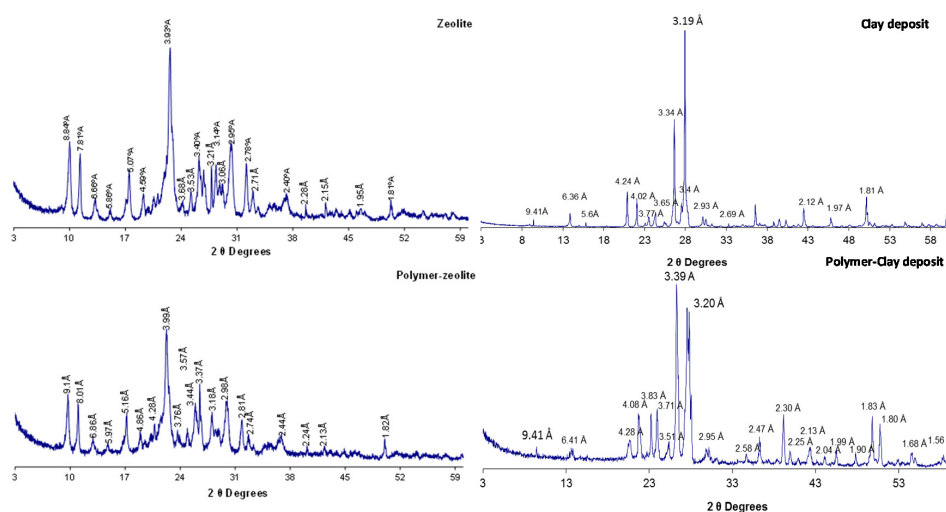


Figure 1. The X-ray diffraction (XRD) analysis of raw and polymerized zeolite and clay deposit.

The functional groups onto the surface of raw and polymerized materials of natural zeolite and naturally occurring local clay deposits were analyzed by means of FT-IR. FT-IR spectra of all investigated materials are presented in Figure 2. For raw natural zeolite, there are bands at 3628.87, 3449.80 cm^{-1} , and 1636.0 cm^{-1} , which are corresponding to a typical stretching and bending of OH groups in water molecules associated with Na and Ca in the zeolite structure. The band corresponding to asymmetry stretch (Si-O or Al-O stretching) in TO_4 tetrahedra appeared at 1065.70 cm^{-1} . The bands at 792.55 cm^{-1} and 467.71 cm^{-1} confirm the presence of symmetry stretch (O-T-O stretching) and T-O stretching, respectively. For the composite of polymer-zeolite, the characteristic absorption peaks at 3187.76 cm^{-1} and 2944.17 cm^{-1} can be attributed to $-\text{NH}_2$ and C-H stretching, respectively. Additional peaks at 1659.54 cm^{-1} (C=O stretching), 1526.47 cm^{-1} (C=C stretching), and 1452.5 cm^{-1} (C-H deformation) were also detected on the surface of the polymerized zeolite.

For clay deposit, there are bands at 3435.19 cm^{-1} and 1622.51 cm^{-1} , which correspond to typical stretching and bending of OH groups. The band corresponding to asymmetry stretch (Si-O or Al-O stretching) in TO_4 tetrahedra appeared at 1004.19–1096.20 cm^{-1} . The bands at 762.96 cm^{-1} confirm the presence of symmetry stretch (O-T-O stretching), and the bands at 418.46 and 460.95 cm^{-1} confirm the presence of T-O stretching. For the composite of polymer-clay deposit, its spectrum shows two bands at 3187.62 and 2944.21 cm^{-1} , which are due to $-\text{NH}_2$ and C-H stretching, respectively. Additionally, the bands corresponding to bond vibrations at 1651.60 cm^{-1} (C=O stretching), 1525.99 cm^{-1} (C=C stretching), 1449.57 cm^{-1} (C-H deformation), and 1311.37 cm^{-1} (C-N stretching) were detected on the surface of the polymerized clay deposit. Compared to un-polymerized samples of zeolite and clay, the characteristic absorption peaks (around 3440 cm^{-1}) of polymerized samples have become strong, mainly due to the amine group ($-\text{NH}$). The FTIR spectra of synthesized composites of polymer-clay through polymerization process have been investigated by several authors [28,29]. Similar to our finding, they found that the stretching vibrations of C-H, C=C, $-\text{NH}_2$, C-N and C=O bonds were detected on the surface-polymerized samples. This indicates that the functional groups interact with clays, and thus, composites of polymer-clay were synthesized.

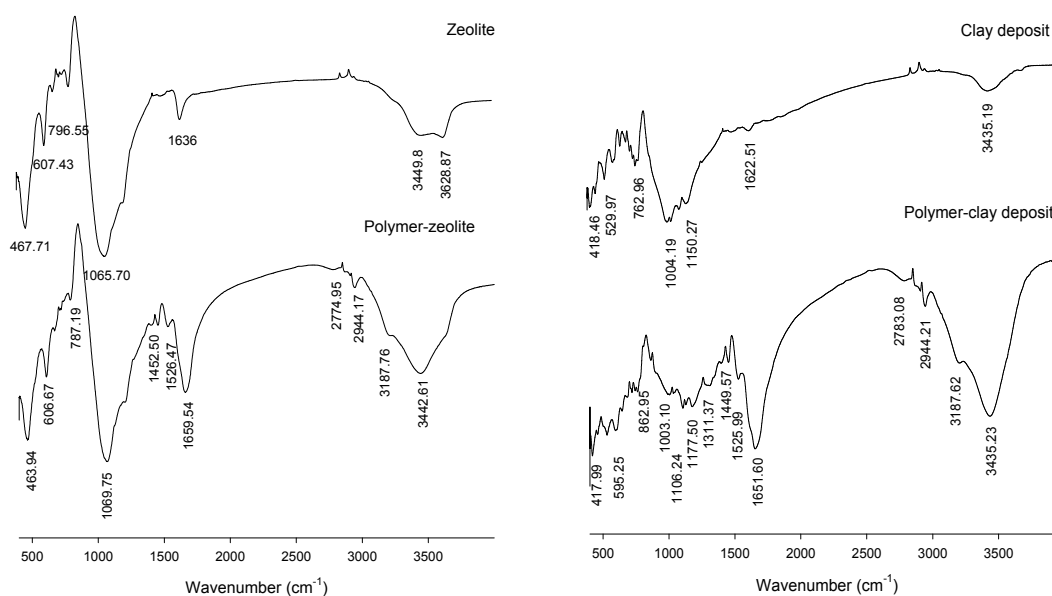


Figure 2. The Fourier transform infrared spectroscopy (FT-IR) spectra of raw and polymerized zeolite and clay deposit.

Figure 3 shows the SEM images for the raw and polymerized zeolite and clay deposit. The SEM images of natural zeolite and local clay deposit after polymerization showed the presence of the large sticking particles with a smooth surface, mainly due to the polymerization process.

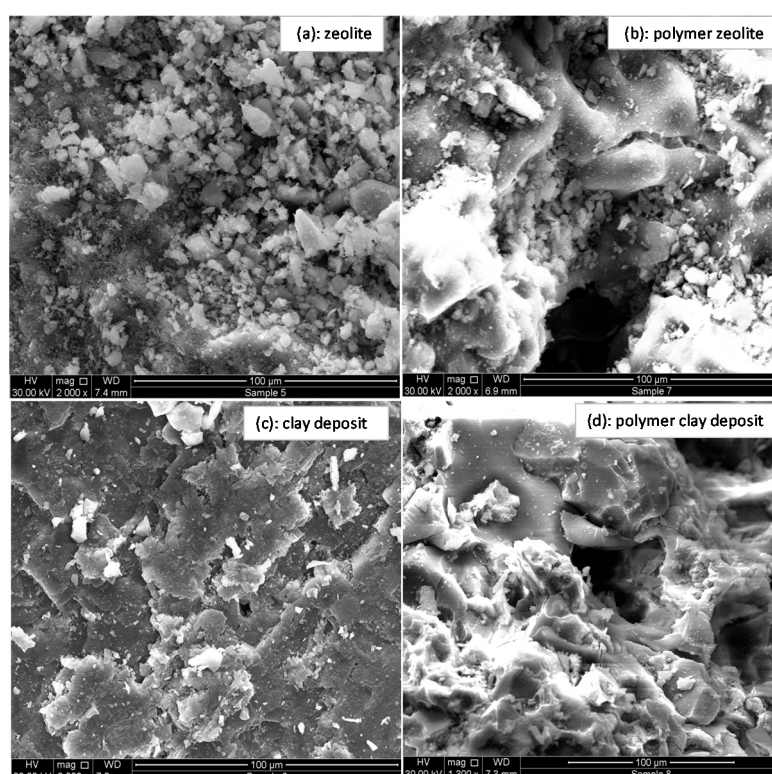


Figure 3. Scanning electron microscopy (SEM) for zeolite (a), polymer zeolite (b), clay deposit (c), and polymer clay deposit (d).

3.2. Adsorption Kinetics and Isotherms

In this study, different kinetics models (pseudo-second order, Elovich, Power function, Parabolic diffusion) were applied on the obtained adsorption data in relation with time to evaluate the kinetics process for Cr(VI) adsorption onto various sorbents. The equilibrium time was pronounced at 5–80 min among various sorbents (Figure 4). The results indicate that the adsorption data were well described by the pseudo-second order kinetic model with the correlation coefficients (r^2) of 0.9996–1.000 for the investigated sorbents (Table 1). Therefore, the pseudo-second order can be applied for predicting the q_e values theoretically for all the studied range of initial Cr(VI) concentrations. Our results suggest that Cr(VI) adsorption onto polymerized and unpolymersed sorbents may be described by chemisorption.

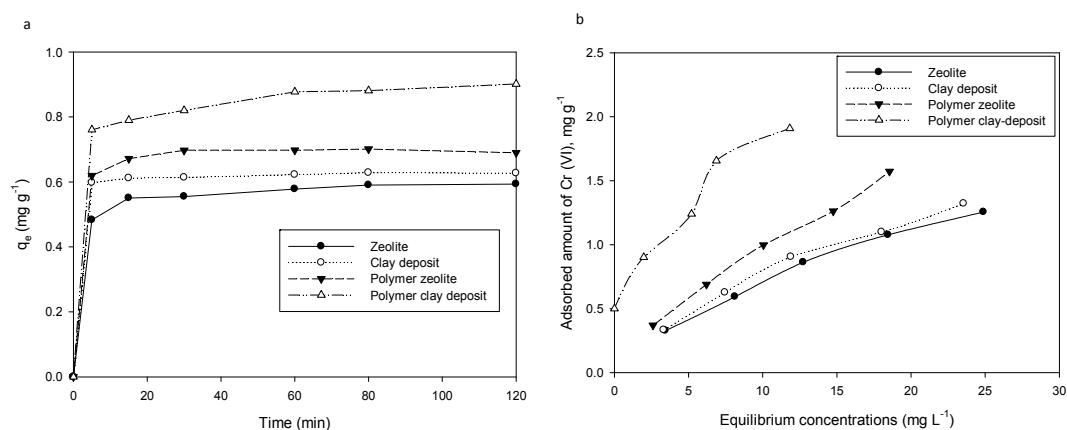


Figure 4. Effect of contact time (a) on Cr(VI) adsorption and sorption isotherm (b) of Cr(VI) by raw and polymerized sorbents.

Table 1. Kinetic model parameters for Cr(VI) adsorption onto the sorbents of raw and polymerized zeolite and clay deposit.

	Pseudo-Second Order				Elovich		Parabolic			Power Function			
	r ²	q _e	h	k ₂	r ²	α	β	r ²	k _{id}	a	r ²	k _f	b
Zeolite	0.9998	0.60	0.35	0.97	0.9338	18,386	29.94	0.815	0.011	0.485	0.9215	0.062	0.449
Polymer zeolite	0.9998	0.70	3.51	7.25	0.7591	4 × 10 ⁹	43.29	0.5523	0.007	0.633	0.7570	0.035	0.601
Clay deposit	1.000	0.63	1.31	3.31	0.9622	2 × 10 ²⁴	104.17	0.8938	0.003	0.595	0.9622	0.016	0.584
Polymer clay deposit	0.9996	0.91	0.40	0.48	0.9648	79,107	21.28	0.9677	0.002	0.727	0.9698	0.057	0.686

The adsorption isotherms show that the adsorption quantity of Cr(VI) on various raw and polymerized sorbents increased with increasing equilibrium Cr(VI) concentrations (Figure 4). The adsorption quantity of Cr(VI) on the polymerized clay deposit followed by polymerized zeolite exhibited higher values than their original samples before polymerization. This finding suggests the potential removal of Cr(VI) using polymerized materials and their higher affinity toward Cr(VI) could be explained by the strong interaction of Cr(VI) with the formed surface groups of polymerized sorbents.

The experimental data on Cr(VI) adsorption were fitted to the all three used models (Langmuir, Freundlich, and Temkin) with the correlation coefficients >0.90 (Table 2). Overall, the correlation coefficient values (r^2) are higher for the Freundlich isotherm (0.9560–0.9987) than for the Langmuir isotherm (0.9232–0.9884) and Temkin isotherm (0.9340–0.9818), suggesting that the Freundlich isotherm model described well the Cr(VI) adsorption onto original and polymerized materials of zeolite and clay deposit. This indicates that Cr(VI) ions are sorbed onto heterogeneous sites with different binding energies. The $1/n$ values of Freundlich model for Cr(VI) adsorption are lower than 1, suggesting a favorable adsorption. Thus, chemisorption can control the adsorption of Cr(VI) onto various raw and polymerized sorbents, indicating a high affinity of Cr (VI) toward the sorbents [30]. The Freundlich constant (K_f), which is generally in relation to the adsorption capacity, showed higher values (0.662) for polymerized clay deposit than those (0.141–0.184) of other sorbents.

Table 2. Langmuir, Freundlich, and Temkin parameters for Cr(VI) sorption onto the sorbents of raw and polymerized zeolite and clay deposit.

	Langmuir			Freundlich			Temkin		
	q_m	K_a	r^2	$1/n$	K_f	r^2	a	b	r^2
Zeolite	2.41	0.043	0.9824	0.692	0.141	0.9961	−0.312	1.10	0.9751
Polymer zeolite	3.33	0.044	0.9360	0.727	0.184	0.9987	−0.279	1.353	0.9497
Clay deposit	2.52	0.045	0.9884	0.700	0.149	0.9929	−0.309	1.144	0.9818
Polymer clay deposit	2.03	0.613	0.9232	0.433	0.662	0.9560	0.461	1.322	0.9340

3.3. Removal Efficiency and Mechanism

The removal efficiency of sorbents for Cr(VI) is presented in Figure 5. The initial solution pH of the 25 mL of an initial Cr(VI) concentration of 25 mg L^{-1} was in a range of 2–10. The results showed that the removal efficiency of Cr(VI) from aqueous solutions was dependent upon initial pH. The highest removal efficiency of Cr(VI) for all the investigated sorbents (raw and polymerized sorbents of zeolite and naturally occurring local clay deposit) was pronounced for the lowest initial solution pH of 2. It has been reported that the sorbents' surfaces that are positively charged are predominant under acid conditions, which are easily attracted toward negatively charged chromium species (HCrO_4^- and $\text{Cr}_2\text{O}_4^{2-}$) [31,32]. Therefore, the maximum removal efficiency was pronounced for a pH value of 2. It was noticed that the removal percentage of Cr(VI) onto various sorbents was 59.3% (raw zeolite), 69.0% (polymerized zeolite), 62.7% (raw clay deposit), and 90.1% (polymerized clay deposit). However, this highest removal efficiency was decreased with increasing initial pH of aqueous solutions and reached 44.6% (raw zeolite), 50.4% (polymerized zeolite), 45.7% (raw clay deposit), and 55.3% (polymerized clay deposit) at the highest initial pH of 10. This behavior suggests that the adsorption process depends

on the dominated species of hexavalent Cr. Previous studies suggested that the monovalent form (HCrO_4^-) dominated at low pH required only a single site on the clay minerals' surface [33]. On the contrary, at high pH values, the divalent form (CrO_4^{2-}) dominated at high pH values required two sites with a positive charge on the surface of clay minerals. Additionally, the excess of OH ions at higher pH is possible to compete with (CrO_4^{2-}), resulting in surprising Cr(VI) immobilization onto the surface of the sorbents. Our results may also suggest that the formed functional groups on the surfaces of sorbents due to polymerization stay in protonation form at acidic conditions, resulting in an increase of the adsorbed chromate quantity. However, as the solution pH increases, the functional groups de-protonation/ionization of the polymerized sorbents tended to occur, resulting in decreasing the adsorbed chromate quantity. It has been previously reported that the adsorption of hexavalent chromium onto the surface of various materials is mainly governed by ion-exchange or outer-sphere complexation at low pH values and by inner-sphere complexation at high pH [34].

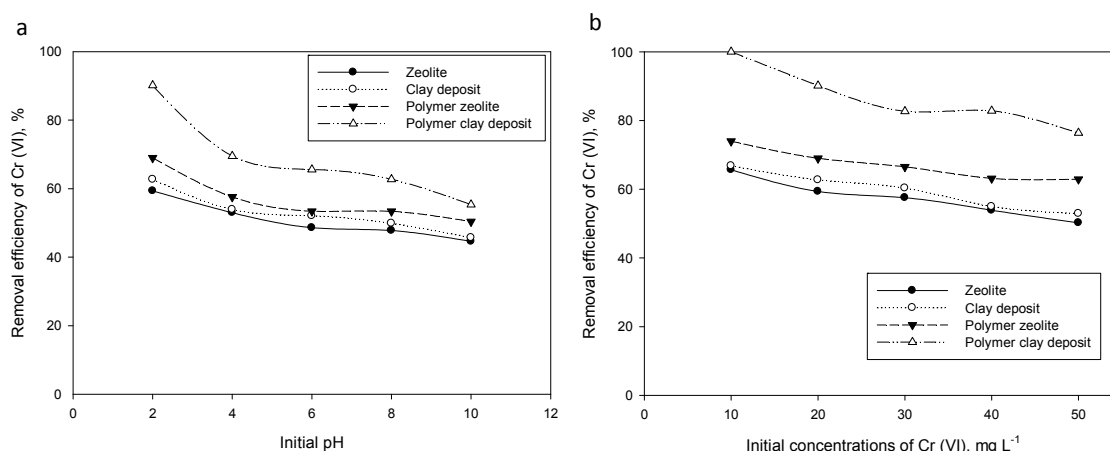


Figure 5. Effect of initial pH (a) and initial concentrations (b) on removal efficiency of Cr(VI) by raw and polymerized sorbents.

The influence of the feed initial Cr(VI) concentrations on removal efficiency by various sorbents of raw and polymerized sorbents of zeolite and clay deposit is shown in Figure 5. It was noted that the removal efficiency of Cr(VI) decreased with an increase in C_i , indicating that the availability of binding sites for Cr(VI) may be occupied, and hence preventing further adsorption of Cr(VI) onto the surface of the investigated adsorbents. It was generally observed that the removal efficiency increased in the following order: polymer clay deposit > polymer-zeolite > raw clay deposit > raw zeolite. The high ability of polymerized sorbents (especially polymerized clay deposit) to remove Cr(VI) from aqueous solutions may be explained by the strong basic nature and high ionization degree of the amine moiety, resulting in sites loaded with positive charges ($\equiv\text{N}^+$) being able to interact electrostatically with anionic forms of Cr(VI) [35]. Several studies have shown that enhancing adsorption capacity of various materials to remove negatively charged ions can be achieved by polymerization process [23,36]. In order to confirm the presence of Cr(VI) on the sorbents, FTIR analysis was conducted before and after the adsorption process (Figures 6 and 7). Comparing the results of the FTIR spectra before and after adsorption onto raw zeolite and clay deposits, some shifts were detected in the stretching vibrations of OH and Si-O or Al-O groups groups (Figure 6). The results of the FTIR spectra before and after the adsorption onto polymerized clay deposits showed a shift in the stretching vibration for the hydrogen bonds of OH at 3435.23 cm^{-1} (before adsorption) to 3431.08 cm^{-1} (after adsorption), for $-\text{NH}_2$ at 3187.62 cm^{-1} (before adsorption) to 3200.36 cm^{-1} (after adsorption), for C-H at 2944.21 cm^{-1} (before adsorption) to 2941.49 cm^{-1} (after adsorption), for C=O at 1651.60 cm^{-1} (before adsorption) to 1659.13 cm^{-1} (after adsorption), and for C-N at 1311.37 cm^{-1} to 1292.26 cm^{-1} upon Cr(VI) adsorption (Figure 7). This confirms that the OH, $-\text{NH}_2$, C-H, C=O, and C-N groups are in connection with the

Cr(VI) adsorption. In addition, there is a shift in the stretching vibrations of OH, C-H, and Si-O or Al-O groups for polymerized zeolite after Cr(VI) adsorption. After Cr(VI) adsorption onto polymerized zeolite, the stretching vibrations of the OH at 3442.61 cm^{-1} , C-H at 2944.17 cm^{-1} and 2774.95 cm^{-1} , and Si-O or Al-O at 1069.7 cm^{-1} are respectively shifted to 3439.15 , 2946.33 , 2879.05 and 1059.32 cm^{-1} . This suggests that these functional groups with several interactions after binding may be responsible for contribution in the process of Cr(VI) adsorption onto polymerized zeolite. Pandey and Mishra [36] suggested that the anionic forms of hexavalent chromium may be adsorbed onto polymer-clay nanocomposite via electrostatic attraction with the functional groups (such as amine).

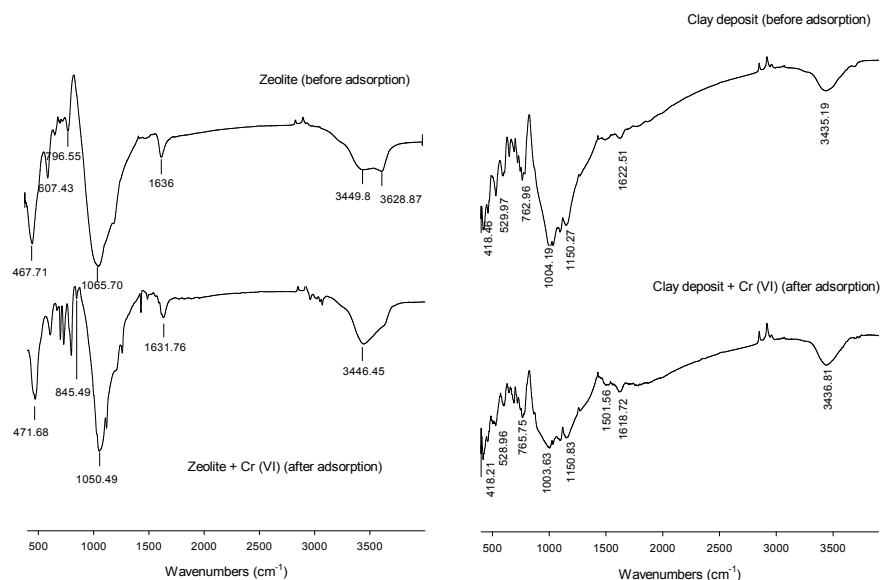


Figure 6. The FT-IR spectra of raw zeolite and clay deposit before and after Cr(VI) adsorption.

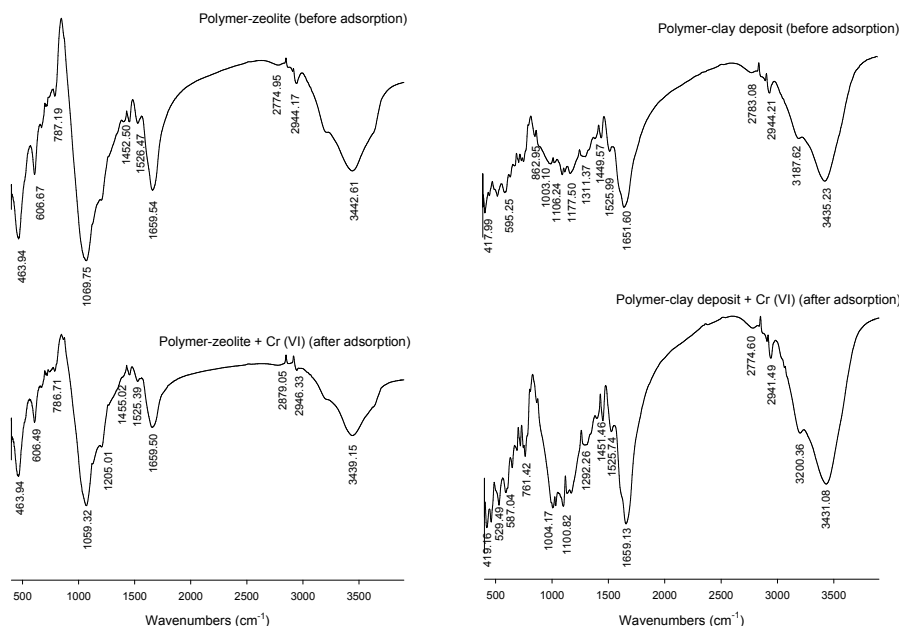


Figure 7. The FT-IR spectra of polymerized zeolite and clay deposit before and after Cr(VI) adsorption.

3.4. Characterization of Tannery Wastewater and Its Treatments Using Polymer Clay

The values of tannery wastewater pH were in the alkaline range (8.32–9.05) mainly due to the alkaline chemicals used in the tanning processes (Table 3). Higher EC values and concentrations of the investigated soluble Na^+ , Cl^- , and SO_4^{2-} in wastewater were observed comparing to standards limit. The high concentrations of these ions may result from the use of significant quantities of their salts in the industry via auxiliary chemicals such as sodium sulphide salts or the salts used in hiding and skin preservation such as chloride salts [2]. Among the investigated heavy toxic metals, the soluble total Cr^{2+} ($195\text{--}878.4\text{ }\mu\text{g L}^{-1}$) of wastewater was very high compared to standards limit [37–39] (Table 3). The presence of high concentration of Cr^{2+} in the wastewater samples of the tannery effluents can be attributed mainly to the addition of significant quantities of chromium salts in the chrome tanning process [2].

Table 3. pH, EC, and soluble ions and toxic heavy metals in tannery wastewater.

	pH	EC dS m^{-1}	Cl	SO_4 mg L^{-1}	Na	Cr	Cd $\mu\text{g L}^{-1}$	Pb
Range (This study)	8.30–9.0	17.5–36.1	3963–11,469	3230–6332	4084–10,210	195–878.4	ND	ND
ISI [28]	6–9	0.85	600	1000	-	-	-	-
NEQS [29]	6–9	0.288	-	-	-	-	-	-
ISW-BDS-ECR [30]	6–9	0.288	-	-	-	100	100	200

ISI [28] = Indian Standard Institute-2000, NEQS [29] = Nature/National of Environmental quality ISW-BDS-ECR [30] = Inland Surface Water in Bangladesh.

Figure 8 presents treatment effects on total soluble Cr^{2+} concentration and percentage of Cr^{2+} removal from tannery wastewater. The removal efficiency of soluble Cr^{2+} increased as the sorbent dose was increased. The highest removal capacities of Cr^{2+} were recorded for polymer-zeolite followed by unmodified one, giving a maximum total chromium removal of 84.4–86.2% at a dosage of $6\text{--}10\text{ g L}^{-1}$ for polymer-zeolite and 83.5% at a dose of 10 g L^{-1} for raw zeolite. Caputo and Pepe [40] found a reduction up to 99.99% of pollutants by using zeolite, depending upon the type of zeolite, charged cations, and the type and concentration of salts in the wastewater.

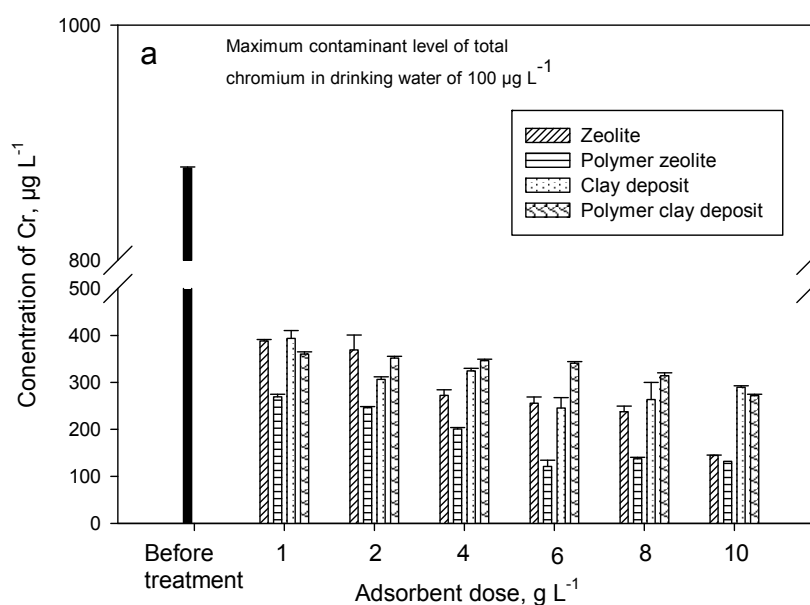


Figure 8. Cont.

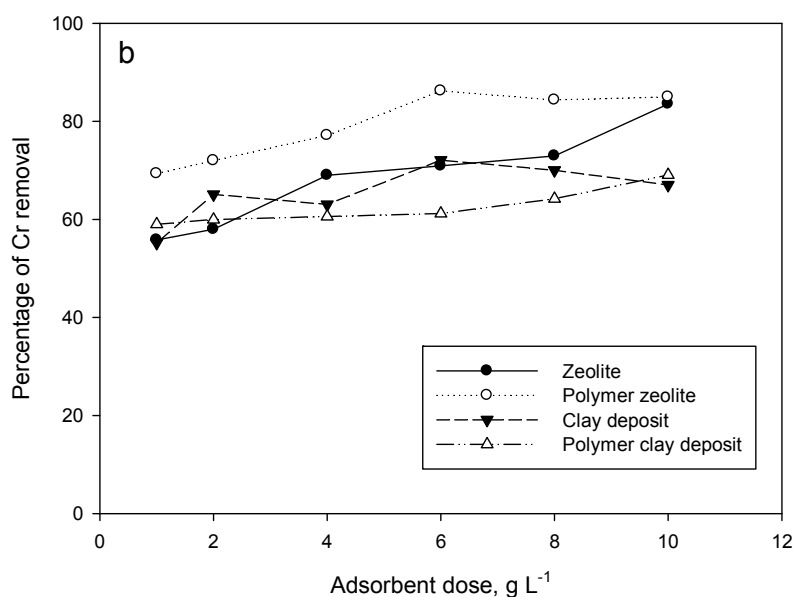


Figure 8. Treatment effects on total soluble Cr^{2+} concentration (a) and percentage of Cr^{2+} (b) removal from tannery wastewater.

A significant low quality of the tannery wastewater is indicated by the high EC values and high concentrations of cations (Na^+) and anions (Cl^- and SO_4^{2-}). Figure 9 shows the effects of raw and polymerized materials on salinity (EC values), and soluble Cl^- , SO_4^{2-} , and Na^+ . Results showed that the salinity was removed from the tannery wastewater to varying degrees. The EC value of in wastewater samples before treatment amounted to $33.3 \text{ (dS m}^{-1}\text{)}$, which was decreased after treatment by 48.9% (raw zeolite) and 55.6% (polymer-zeolite) and 56.7% (raw clay deposit) and 57.1% (polymer clay deposit).

The results showed that the ions of Cl^- , SO_4^{2-} , and Na^+ on the studied sorbents are retained (Figure 9). The removal percentage of Na^+ ions onto various sorbents was 32.7% (raw zeolite), 65.2% (polymer-zeolite), 55.7% (raw clay deposit), and 67.4% (polymer-clay deposit). The removal percentage of Cl^- ions onto various sorbents was 33.7% (raw zeolite), 63.1% (polymer-zeolite), 56% (raw clay deposit), and 65.8% (polymer-clay deposit). Meanwhile, the removal percentage of SO_4^{2-} ions onto various sorbents was 60.8% (raw zeolite), 88.6% (polymer-zeolite), 87.9% (raw clay deposit), and 92.6% (polymer-clay deposit). The retention of different ions on zeolite and clay minerals or mineral-containing materials may be a reasonable reason for reducing the electrical conductivity. In addition, the precipitation process may lead to a reduction of the concentration of dissolved salts. According to numerous studies conducted by a number of researchers [40,41], the use of zeolite may be highly efficient in wastewater purification and desalination. Zhao et al. [41] reported that ammonium reduction in the municipal water sanitation reached 89.8% using zeolite. In a study by Ghaly and Verma [42] on the water from the sludge saltwater desalination by ion exchange column of zeolite, the efficiency of removal of sodium salts amounted to 75.34%. In the current study, the highest removal capacities of Na^+ , Cl^- , and SO_4^{2-} were recorded for polymer-clay deposit, followed by polymer-zeolite. The findings of the current study suggest that the polymerized materials of clay deposit or zeolite may be employed as highly efficient sorbents for the removal of toxic ions from the wastewater.

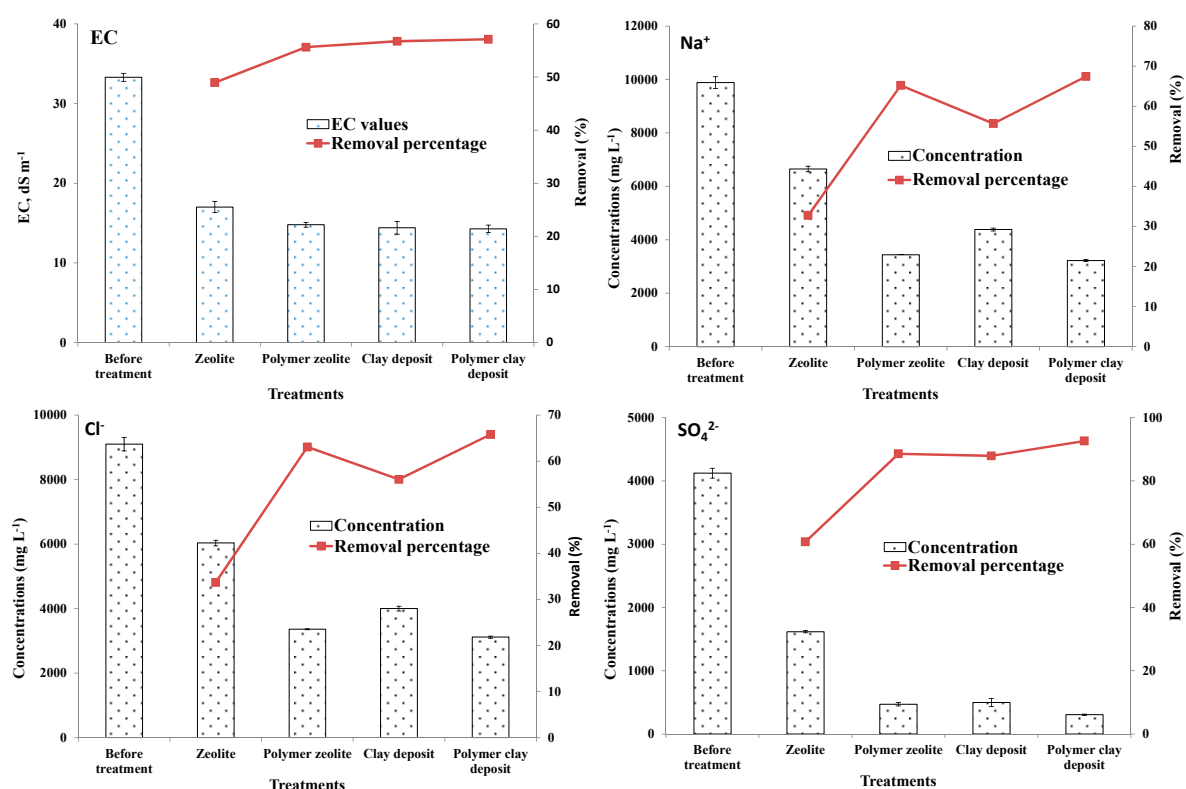


Figure 9. Treatment effects on soluble EC values, and the concentrations of soluble Na⁺, Cl⁻ and SO₄²⁻ of tannery wastewater.

4. Conclusions

The results of this study indicated that the tannery wastewater contained very high values of EC, soluble Na⁺, Cl⁻, SO₄²⁻, and Cr²⁺. Our findings showed that the highest removal of Na⁺, Cl⁻, and SO₄²⁻ from tannery wastewater was recorded for polymer-clay deposit, followed by polymer-zeolite. However, the highest removal of soluble Cr²⁺ from tannery wastewater was recorded for polymer-zeolite. For removal of Cr(VI) from aqueous solutions, the highest removal efficiency was produced by the polymer-clay deposit composite. Our findings also suggest that the environmental assessment of tannery effluents should be taken into account, and their treatment using modified sorbents is necessary for preventing pollutants from entering the environment.

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