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Experimental Study on the Removal of Chromium (III) Ions Using Synthesized Reduced Graphene Oxide (RGO)

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Article

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ABSTRACT

Tanning industries release chromium-based effluents directly into the environment putting the whole ecosystem at risk. As a result, the wastewater must be properly treated before being released. Reduced Graphene oxide (RGO), a graphene material having adsorption capacity, is prepared, characterized, and applied to Chromium (III) effluent (synthetic effluent-SE) to determine its efficiency and adsorption capacity (AC). RGO was characterized by TGA, SEM images, XDR, and FTIR analysis. It was a well-developed adsorbent because of its high thermal stability, wrinkled topology, the disappearance of broad peak at 2-theta angle 10.049° present in GO, and the presence of oxygen-containing functional group respectively. A batch experiment has been carried out at different adsorbent doses, contact times, and pH on the effluent. About 90.31% removal efficiency was found within 10 minutes when the absorption capacity was 180.61mg/g. Therefore, isotherm and adsorption kinetics of chromium ions on the RGO surfaces were studied to understand the different aspects of adsorption capability. The result showed that the process was favourable for adsorption. RGO suggested monolayer adsorption because it followed the Langmuir Isotherm more closely than the Freundlich isotherm model. Additionally, it was more compatible with the intraparticle diffusion (IPD) and pseudo-second-order (PSO) models. The findings demonstrated that RGO has great potential as an adsorbent for efficiently and swiftly removing chromium ions from wastewater.

KEYWORDS

RGO, chromium, adsorption, kinetic, isotherm

INTRODUCTION

The industrial tanning process involves a reaction between chrome salt and leather by engaging about 60-70% inside the leather and about 40-30% discharged into the environment as a solution [1]. Chrome leaching or direct discharge of chrome waste can affect the soil and aquatic system through chemical reactions such as hydrolysis, oxidation-reduction, and precipitation [2]. Chromium is released from the industry in the Cr^{3+} ion form, where it can be converted into a Cr^{6+} ion form under a required condition which is very dangerous for humans. It is deemed carcinogenic and can harm human organs including the kidney, liver, skin, and gastrointestinal system since it can convert into a more toxic Cr (VI) state

[3]. Human health may be affected through inhalation and food and may cause health problems such as a weakened immune system, allergic reactions, kidney and liver damage, skin rash, nosebleed and irritations, ulcers, change in genetic configuration, and possibly even death varying person to person [4].

There are many methods which are used to remove chromium ions like chemical precipitation, electrochemical, physical and biological treatment, and adsorption [3]. Chemical precipitation is one of the most used methods for removing chrome from a tannery that involves the reaction between chrome liquor and alkali or base which increases the salinity of water and produces toxic gases and residual sludge [5]. Though Electrochemical treatment has created lots of interest among researchers, it requires a highly maintained environment to operate [6]. Another sustainable traditional method for removing this pollutant is bioremediation which uses biological organisms but the process takes much longer time to remove the contaminant [7]. Adsorption, another way of removing metal ions, has been used for a long time because of its unique features depending on the particular adsorbent. For example, Chitosan, a cheaper, and green adsorbent showed an effective adsorption capacity (138 mg/g) to remove the Cr^{3+} ion because it carries amino ($-\text{NH}_2$) and hydroxyl ($-\text{OH}$) group including some limitations such as column clogging, experimental setup [8].

Various nanoparticles, nowadays, are used as adsorbents showing an alternative path for removing heavy metals and the prime reasons are the size (smaller) and surface area (larger) of the adsorbent. In addition, the mobility is high in solution and it can effectively remove pollutants from wastewater [9]. An experiment carried out in removing trivalent chromium through bare magnetic Fe_3O_4 nanoparticles reached high adsorption capacity (355.55 mg/g) when the pH was more than 6 which indicates the solution was going on in basic condition [10]. After that pH, chromium begins to precipitate usually. Crosslinked polymethyl methacrylate nanocomposites with SnO_2 can remove Cr^{3+} ions within one hour at pH 6 where 1.76 mg/g adsorption capacity was achieved [11].

Graphene oxide (GO), a popular graphene-based material, facilitates the absorption of organic as well as inorganic materials through its basal plane and oxygen-containing functional groups like hydroxyl ($-\text{OH}$), alkoxy ($\text{C}-\text{O}-\text{C}$), carboxylic ($-\text{COOH}$), and carbonyl ($-\text{CO}$) groups [12]. It provides large surface area with excellent physical and mechanical properties and good chemical stability [13]. Reduced Graphene Oxide (RGO), containing less oxygen functional group compared to GO, allows the absorption of heavy metals to the negatively charged active sites in the available largest RGO interlayer spacing [14,15]. Many functionalized RGOs have already shown a greater removal percentage with high adsorption capability in removing heavy metals such as Hg (II), Pb (II), Cu (II), Cd (II), and Ni (II) [16,17]. Another study carried out on trivalent Antimony where 3D-reduced GO/sodium alginate double network (GAD) is used and found 7.67 mg/g adsorption capacity [18].

Globally, however, most tanneries are discharging chromium-containing wastewater directly into the environment without proper treatment and putting human society in danger [19]. In third-world countries like Bangladesh, this situation is harming leather selling in the world market. To overcome this problem, adsorption can be an option. Although many studies are based on GO or RGO composites in removing chromium ions, RGO (reduced by L-ascorbic acid sodium salt) has not been used directly. This study aims to reduce the environmental impact created by Cr^{3+} ions from tannery effluent. So, in this experiment, RGO has been applied as an adsorbent to find out its effectivity in chrome-containing water and to achieve good removal efficiency (RE) and adsorption capacity (AC).

MATERIALS AND METHODS

Chemicals

The chemical and reagent, employed in the experiment, were all analytical grades without further purification. Graphite powder, the raw material for making RGO, was purchased from Loba Chemie Pvt Ltd. (98% extra pure). Other chemicals and reagents were Sulfuric acid (H_2SO_4 , 98%), Sodium Nitrate (NaNO_3 , 98% extra pure), Potassium permanganate (KMnO_4), Nitric Acid (HNO_3), Ammonia Solution (NH_3 , 25% pure), Hydrogen peroxide (H_2O_2), L Ascorbic Acid Sodium salt ($\text{C}_6\text{H}_7\text{NaO}_6$). The Synthetic Effluent (SE) has been produced using deionized (DI) water and Chromium (III) Sulphate $\{\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}\}$ for the treatment.

Analytical Instruments

For Thermogravimetric analysis (TGA), PerkinElmer, TGA 8000 was operated by inserting about 3 mg to 6 mg sample into the machine and heated in a furnace purged in between 50-800 °C temperature with an inert atmosphere. Scanning Electron Microscopy (SEM) and X-ray diffraction Analysis (XRD) have been conducted by SEM (JEOL, JSM-6490) and X-ray Diffractometer (Ultima) (10-70° angle). The Fourier-Transform Infrared Spectroscopy analysis (FTIR) has been performed between 4000 cm^{-1} and 400 cm^{-1} wavelengths by Shimadzu, IR Prestige21 instrument. To determine the heavy metal amount, the Atomic Absorption Spectrometry (AAS) machine (PerkinElmer, PinAAcle 900H) has been used.

Graphene Oxide (GO) Preparation

Before producing RGO, GO was synthesized using a modified Hummers method [20]. Sodium nitrate (2 g) and H_2SO_4 (98%, 90 mL) were combined with 2 g of graphite powder and stirred for 4 hours in a 1000 ml beaker inside an ice bath. 12 g of KMnO_4 was progressively added while maintaining this solution below 10 °C and stirring for an additional 2 hours. It was agitated (2 hours) at 35 to 40 °C after the ice bath was removed, then slowly mixed with 184 mL of deionized (DI) water and heated to 98 °C

until it became brown colour. More DI water (200 mL) was added and stirred was continued for 2 more hours. By adding 40 mL of 30% H₂O₂ solution and repeatedly rinsing with 10% HCl to remove metal ions, the reaction was stopped. The process was repeated until the pH was neutral.

Reduced Graphene Oxide (RGO) Preparation

To reduce GO, Ascorbic acid is a useful reducing agent. In the present study, L-ascorbic acid sodium salt was used. Solely, 1 g GO was taken in a 1000 ml beaker and 1000 ml DI water was added to make 0.1 mg/mL solution. L-ascorbic acid sodium salt (5 g) was added. To ensure colloidal stability throughout the electrostatic repulsion, the solution pH was raised to 10 by adding ammonia solution (6 mL) and stirring (2 hours) at 60 °C. RGO powder was obtained by washing the resulting suspension and letting it dry for another 24 hours at 60 °C.

Synthetic effluent (SE) Preparation

The aqueous solution of Chrome sulfate [Cr₂(SO₄)₃.6H₂O] was named as a Synthetic Effluent (SE) in this experiment. The molecular weight of the chrome sulfate was 500 g. A solution of 20 ppm was made at room temperature which was 25±2 °C. SE was then prepared for conducting tests with adsorbent against different parameters such as chromium concentration, pH, and different time durations. Various concentration of chrome sulfate solution was prepared through the equation 1:

$$S_1V_1 = S_2V_2 \quad (1)$$

Where S₁ and S₂ express concentration and V₁ and V₂ are indicated volume.

Adsorption Study

RGO was utilized to treat SE through a batch experiment remembering all the conditions required for the adsorption kinetics study and isotherm model. All the experiments were performed in a 250 ml conical flask at room temperature (25±2 °C). Shaking was operated at 260 rpm. NaOH and HNO₃ were used to adjust the pH in the effluent. About 50 ml of prepared effluent was taken for studying the adsorption studies. After each experiment, the effluents were filtered and tested in atomic absorption spectroscopy for Chromium detection. For batch absorption, different doses of RGO (2, 3, 5, 7, 10, and 20 mg) were first applied to the SE (50 mL) at pH 5. Then, various times and pH were introduced to evaluate the effects. After equilibrium, 5 mg of RGO was applied to the samples carrying different concentrations (20, 30, 40, 50, and 60 ppm) to determine the kinetics and isotherm. Equations 2 and 3 were used for determining the adsorption capacity and percentage of chromium (III) ion removal.

$$Q_e = \{(C_o - C_e)/m\} * V \quad (2)$$

$$\%R = \{(C_o - C_e)/C_o\} * 100 \quad (3)$$

Where: the volume of the aqueous solution (L) and dry weight of the adsorbent (g) are indicated by V and m respectively: Q_e state the equilibrium adsorption capacity (mg/g), C_o and C_e are the initial concentration (mg/L) and equilibrium concentration (mg/L) of metal ions in solution respectively.

RESULT AND DISCUSSION

Characterization of Reduced Graphene Oxide

Figure 1(a) and (b) depict the thermodynamic stability of GO and RGO respectively. It also provides information about DTG. In terms of RGO, it was found to be much more thermally stable than GO. A sharp decrease of 22% was observed in the TGA curve of GO from 50 °C to 168 °C due to the elimination of water molecules from the GO lattice [21].

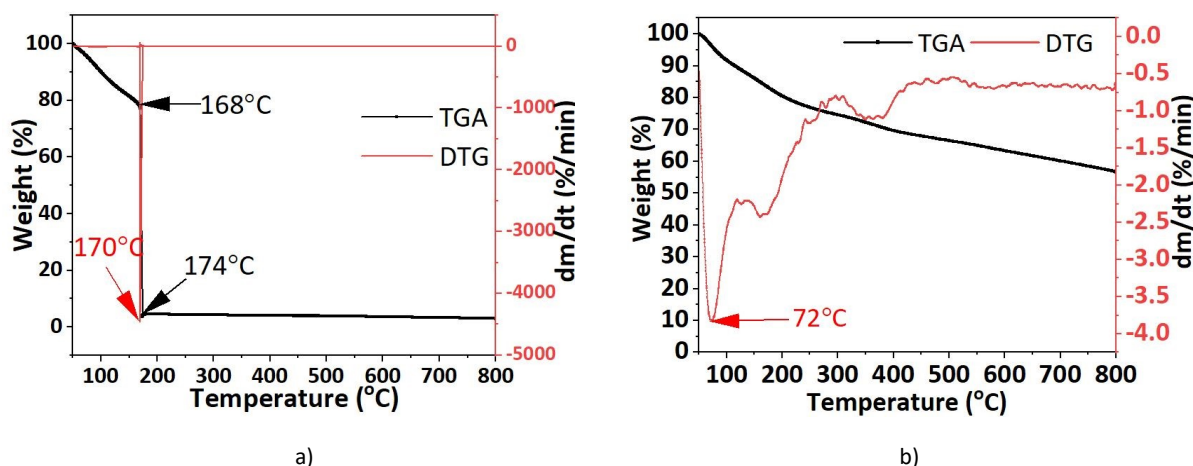


Figure 1. (a) TGA and DTG of GO; (b) TGA and DTG of RGO

But there was a sudden weight loss of 74% occurred from 168 °C to 174 °C as oxygen-containing functional groups were removed during the combustion process. Turning on the DTG graph of GO, the maximum weight change happened at 174 °C. The temperature increment from 50 °C to 200 °C in the RGO-TGA curves provided information about a weight loss of 20%. A small amount of water may have passed away at that temperature. Furthermore, the temperature increased to 800 °C when 46% weight loss happened. Because of the pyrolysis of the functional groups on the materials' surfaces that contain oxygen, the weight loss was slower and more gradual along the curve. In comparison to GO, RGO showed a fluctuating curve at different levels where the maximum degradation temperature was

72 °C. Finally, the TGA graph shows that RGO is more stable than GO.

The XRD pattern of GO and RGO is exhibited in Figure 2(a). A broad peak was observed at a 2-theta angle of 10.049°, indicating a 0.88 nm interlayer distance. It revealed a greater distance between the GO layers than the layers of graphite (0.34 nm) due to the presence of the functional group. The broad peak (observed in GO XRD images at a 2-theta angle of 10.049°) disappeared in RGO. This incident indicated a partial decrease in GO. However, a large peak at diffraction angle $2\theta = 25.59^\circ$ was identified, which suggests a smaller interlayer spacing of 0.35 nm. It may have happened due to the reuniting of the RGO sheets after the elimination of absorbed water [17].

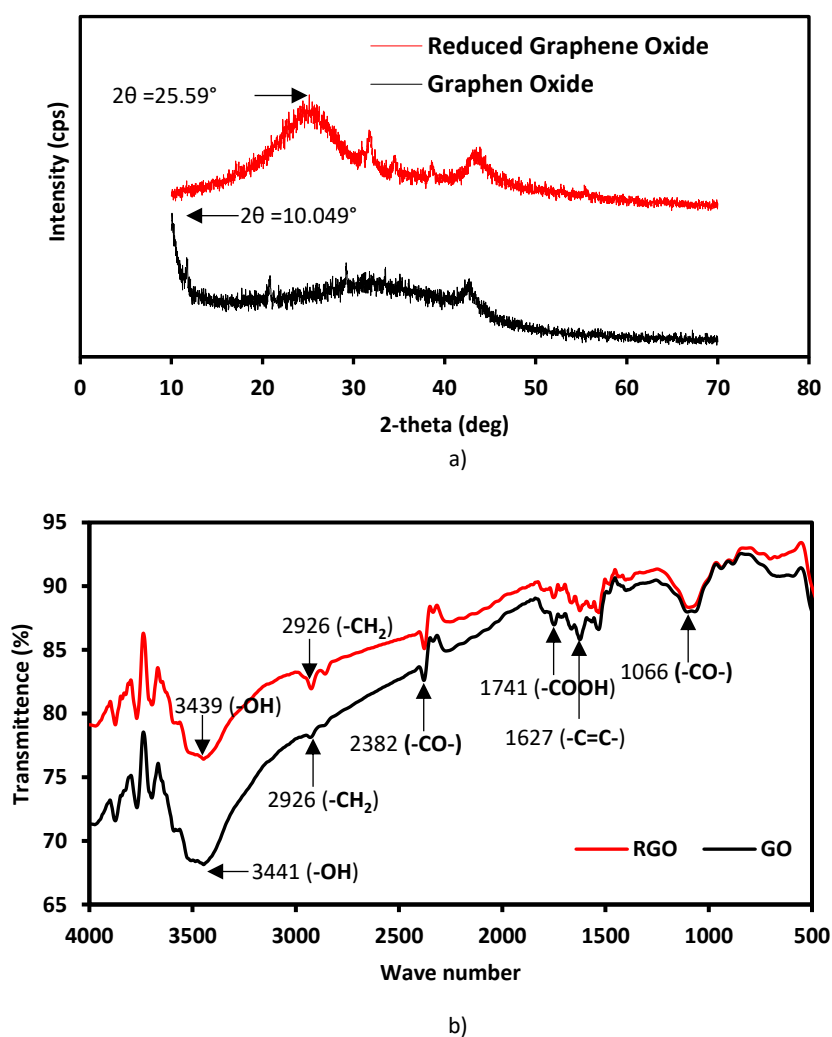


Figure 2. (a) XRD images of GO and RGO at different fraction angles; (b) FTIR of GO and RGO

Figure 2(b) represents the FTIR spectroscopy which determined different functional groups. The hydroxyl (-OH) group's stretching vibration was represented by an intense peak in the FTIR spectra of GO and RGO at 3441 cm^{-1} and 3439 cm^{-1} , respectively. The stretching modes of the carboxyl group (-COOH) and alkoxy group (-COC-) of the sp^2 carbon skeletal body were represented by other lower

intensity peaks at 1741 and 1066 cm^{-1} , respectively [17,20-22]. The intense peak in GO at 1627 cm^{-1} indicates the C=C skeleton of graphite [23]. Two additional peaks were observed at 2926 cm^{-1} and 2858 cm^{-1} wavelength because of the stretching mode of methyl group ($-\text{CH}_2$) in the alkyl chain [22].

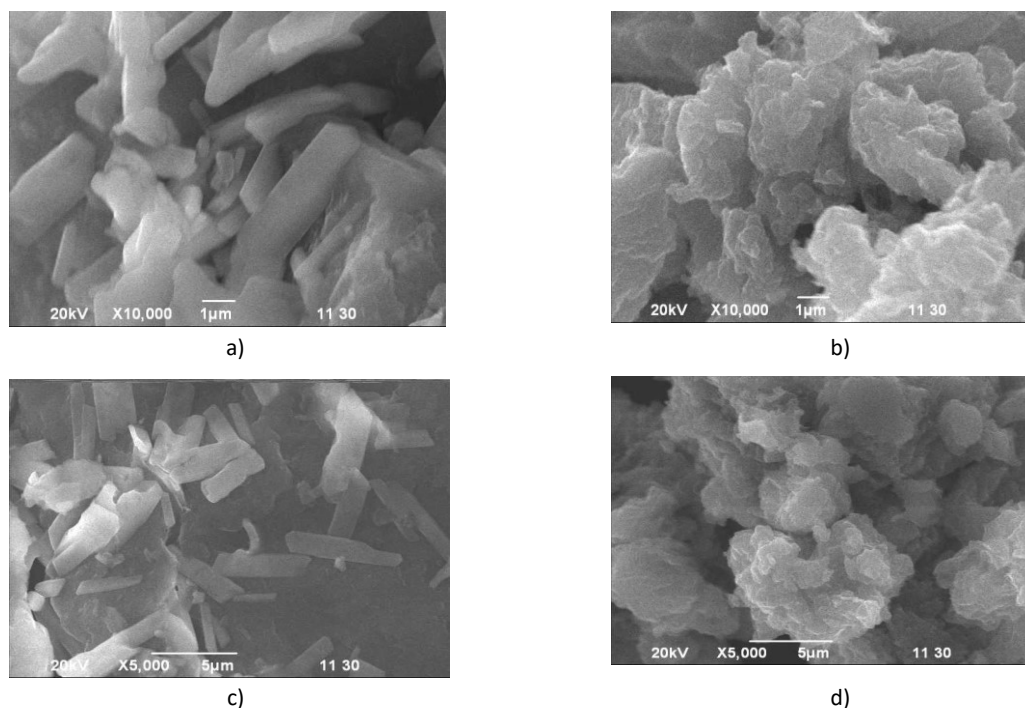


Figure 3. SEM picture of GO (a) at 10000 magnifications, RGO (b) at 10000 magnifications, GO (c) at 5000 magnifications and RGO (d) at 5000 magnifications

Figure 3 displays the SEM pictures of the GO (a), (b) and RGO (c), (d) at 10000 and 5000 magnifications. The images of GO showed a layered flake and wrinkled surface because of the interactions between surfaces, and functional groups that contain oxygen. It was found that nanosheets were not completely isolated from one another and agglomeration was still present at a tiny scale. Therefore, such a layered flake provides evidence of full oxidation of graphite. In terms of the SEM image of RGO, it illustrated that the sample had randomly aggregated, rougher wrinkled topology, and folded. Additionally, separation of various layers was found in the images, and the figures showed no agglomeration.

Chemistry of GO, RGO, and Adsorption Mechanism

Graphite is oxidized to make GO [24]. The reduction of GO by ascorbic acid is an economical, non-toxic, and environment-friendly process [25]. The probable bonding mechanisms between RGO and chrome ion are given in Figure 4 [26]. The adsorption can occur in two different ways. It can happen on the surface of the RGO layer and in between two layers.

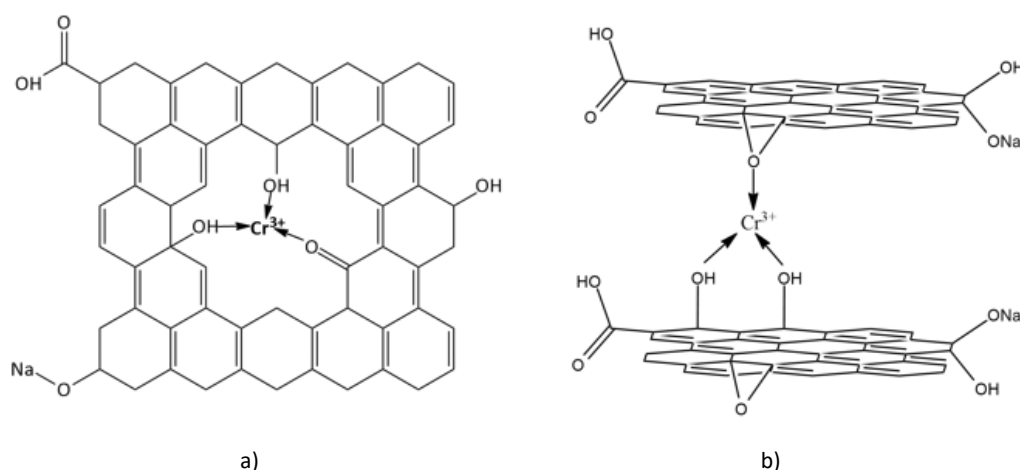


Figure 4. Different types of bonding schemes of RGO and Chromium ions

Due to the presence of a sodium ion in the L-Ascorbic Acid Na salt molecule, it may be occupied in the functional groups that contain oxygen in the GO layer. These groups are the primary factors causing the adsorption of heavy metals in the context of the GO adsorption mechanism [14]. Moreover, it provides an available number of negatively charged active sites for positively charged Chromium ions. However, the available high number of active sites of GO creates some difficulties in metal diffusion. The interstitial diffusion of chromium (III) ion to active species is facilitated by the larger interlayer spacing of RGO [15].

Adsorbent doses and pH effect on chromium ion

Figure 5 (a), and (b) illustrates the Adsorbent Dose compared to removal Efficiency (RE) and Adsorption Capacity (AC). A significant removal efficiency (RE) of approximately 96.02% was achieved when the adsorbent dose was only 20 mg. But much better performance in terms of adsorption capacity (AC) and removal efficiency was seen for 5mg of RGO, where RE and AC were found 83.36% and 416.80 mg/g respectively.

RE and AC curves at various pH have been displayed in Figure 5 (c), (d). Generally, the chrome liquor is in an acidic condition (around pH 4) after chrome tanning. On the other hand, in basic conditions, chromium starts to precipitate slowly. In this study, the batch absorption was done up to pH 9. After pH 6, it was observed that the removal efficiency was above 99%. However, the result was found well for the efficient removal of Cr^{3+} at pH 5 which is near to the native effluent pH value while removal efficiency and adsorption capacity are 90% and 180.61 mg/g respectively.

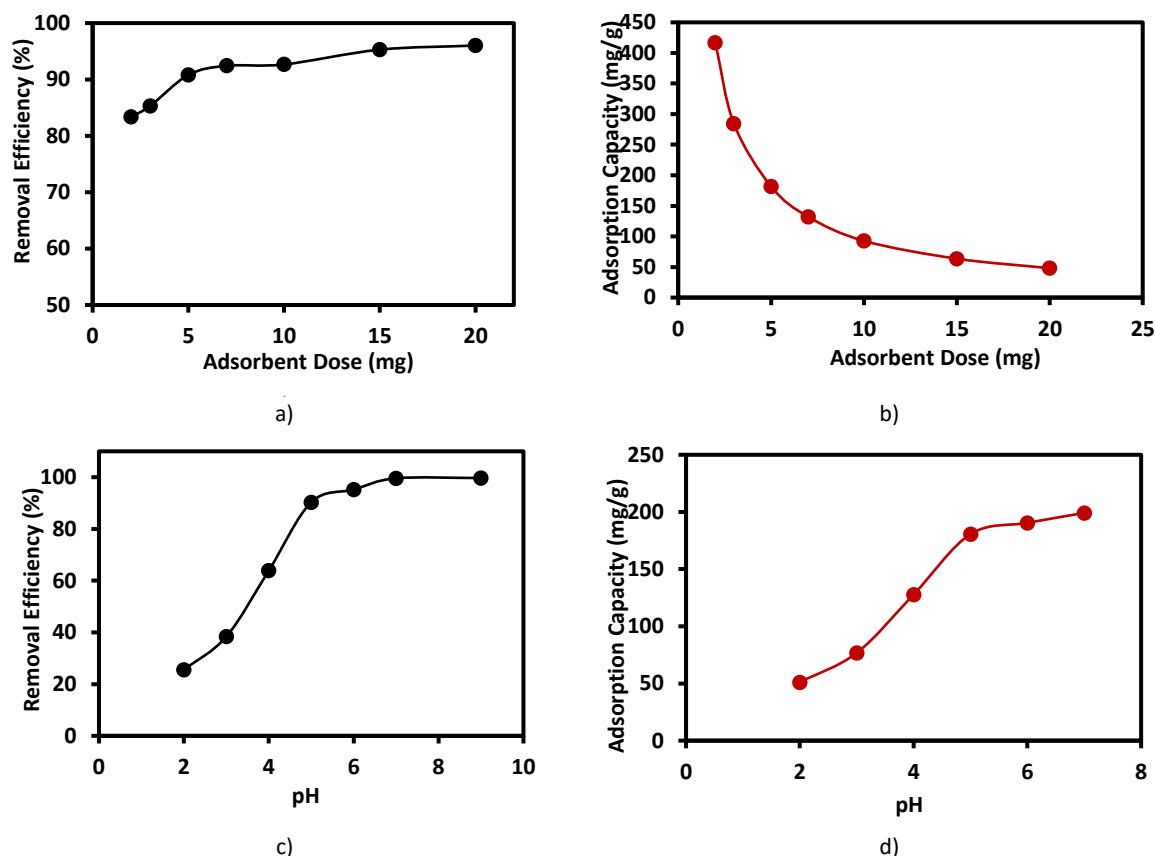


Figure 5. Relation between (a) dose compared to adsorption capacity and (b) dose compared to removal efficiency; Relation between (c) pH compared to adsorption capacity and (d) pH compared to removal efficiency

Isotherm Model

Isotherm models are the simplest and most useful way to find out the adsorbate (RGO) molecules distribution in different phases (solid or liquid). To determine important details like the adsorption mechanism, the affinity between the adsorbate and the adsorbent, and the favorability of the adsorption process, the data from the experiment have been fitted with the Langmuir and Freundlich isotherm model [27].

The Langmuir isotherm model, which is restricted to monolayer adsorption, is represented by the equation 4 below [28]:

$$Q_e = (Q_m * K_L * C_e) / \{1 + (K_L * C_e)\} \quad (4)$$

Where Q_e (mg/g) and Q_m (mg/g) are the amount of metal adsorbed per particular amount of adsorbent and the maximum number of metal ions necessary to produce a monolayer respectively; C_e (mg/L) indicates the equilibrium concentration. The linear Langmuir model depicted in Figure 6 (a) can be used to derive the values of Q_m and K_L . Equation 5 shown below can be used to calculate K_L , also known as the Langmuir constant:

$$(C_e/Q_e) = \{1/(Q_m * K_L)\} + (C_e/Q_m) \quad (5)$$

In Figure 6 (a), values of C_e/Q_e against C_e have been displayed. Langmuir isotherm data which is shown in Table 1 with intercept and slop, were used to calculate the Q_m and K_L values. Correlation coefficients (R^2) were determined for the effluent (0.99) indicating monolayer adsorption into the RGO as the values close to one. The Q_m values for the effluent were 208.33 mg/g.

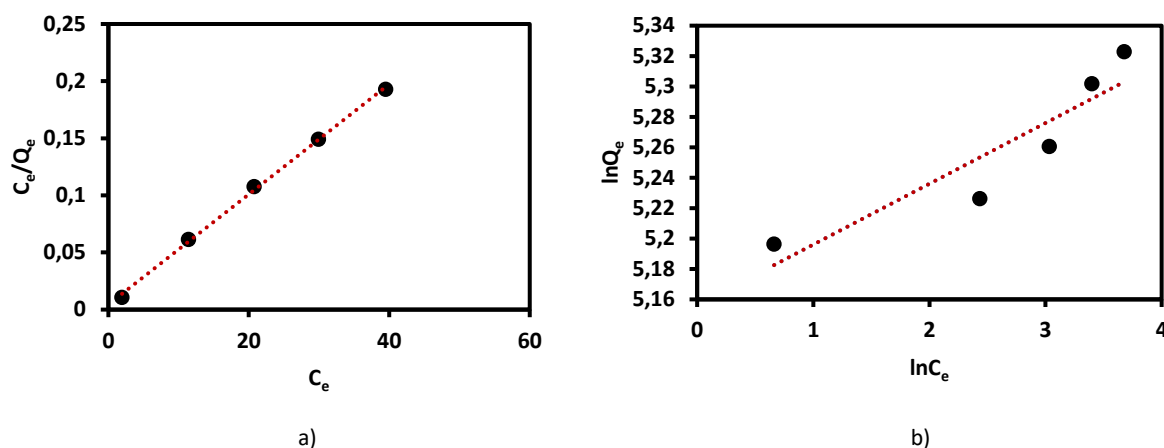


Figure 6. (a) Langmuir Isotherm model; (b) Freundlich Isotherm model

The Freundlich isotherm model indicates multilayer adsorption with heterogeneous surfaces and is not confined to monolayer adsorption, as shown by the following equation 6:

$$Q_e = (K_F * C_e^{(1/n)}) \quad (6)$$

The form of the equation 7 is as follows in its linear version [29]:

$$\ln Q_e = \ln K_F + \{(1/n) * \ln C_e\} \quad (7)$$

Where Q_e (mg/g) indicates metal uptake at equilibrium state; sorption capacity measurement or Freundlich isotherm constant is denoted by K_F ; n expresses the adsorption intensity, and lastly the final or equilibrium concentration is indicated by C_e (mg/L). The linear Freundlich isotherm model was studied using the data by graphing the $\ln C_e$ value against the $\ln Q_e$ value in Figure 6 (b). The n and K_F values are calculated and collected in Table 1. The Freundlich shows a lesser correlation coefficient value (0.84) than the Langmuir isotherm (0.99) indicating more monolayer adsorption. The K_F value (173.45 mg/g) is found lower than the experimental value (180.61 mg/g) showing a lower adsorption rate.

Table 1. Values of different parameters from the isotherm model

Model	Parameter	Value
Langmuir	K_L (L/mg)	1.09
	Q_m (mg/g)	208.33
	R^2	0.99
	K_F (mg/g)/(L/mg) ^{1/n}	173.45
Freundlich	n	25
	R^2	0.84

Contact time and kinetics

At different contact times, batch adsorption was carried out and the results showed that it required only a few minutes to take good adsorption. The results are depicted in Figure 7 (a) showing a high adsorption rate when 89% removal efficiency is achieved within 5 minutes. After that, the rate was slow and the operation was conducted for 2 hours and it made a slight increase in removal efficiency (92%). The equilibrium time for the next step was determined to be two hours of contact time.

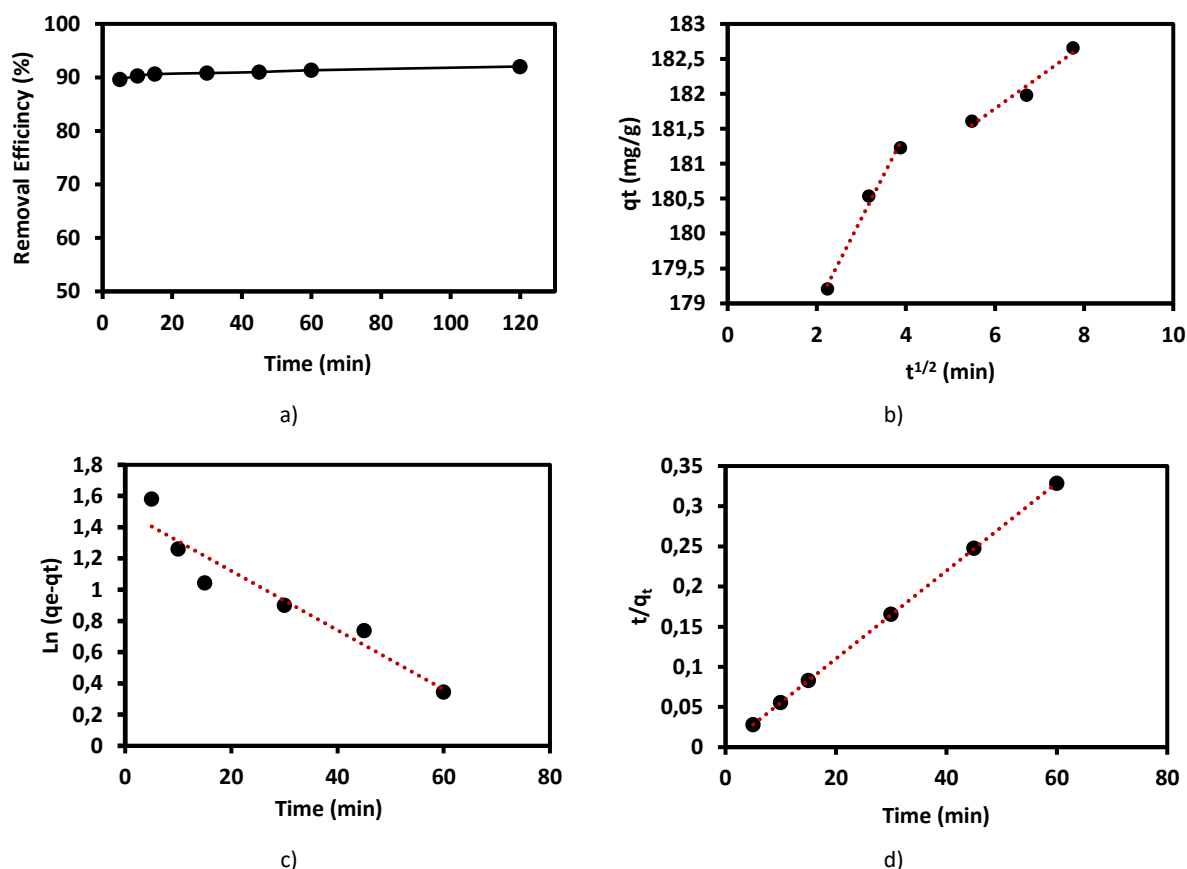


Figure 7. (a) Relation between contact time compared to removal efficiency; (b) Intraparticle diffusion (IPD); (c) pseudo-first-order (PFO); (d) pseudo-second-order (PSO)

Therefore, the intra-particle diffusion (IPD), pseudo-first-order (PFO), and pseudo-second-order (PSO) models, which are shown in Figure 7 (b), (c), and (d), respectively, are used to investigate the adsorption kinetics of Cr^{3+} on RGO surfaces. Using Equations (8), (9), (10) and (11) respectively, the corresponding linear forms of these models are determined.

$$q_t = (k_p * t^{(1/2)}) + C \quad (8)$$

$$\ln(q_e - q_t) = -k_1 + \ln(q_e) \quad (9)$$

$$(t/q_t) = \{1/(k_2 * q_e^2)\} + (t/q_e) \quad (10)$$

$$h = (k_2 * q_e^2) \quad (11)$$

In the above equation, the equilibrium time, and adsorption capacity at time “t” are denoted by q_t and q_e (mg/g), respectively. Herein, k_1 (1/min) and k_2 {(min*g)/mg} indicate the pseudo-first-order and pseudo-second-order rate constants, respectively. The primary adsorption rate (h) from the pseudo-second-order kinetic equation is determined by equation 11. Moreover, the k_p {(min^(1/2) *mg)/g} and C express the value of the IPD rate constant and intercept, respectively. Table 2 lists the kinetic parameters, including the correlation coefficient (R^2).

Table 2. Values of different parameters from the kinetic model

Model	Phase State	Parameter	Value
Intra-particle diffusion	Phase 1	$K_p \{(\text{min}^{(1/2)} * \text{mg})/\text{g}\}$	1.24
		C	176.48
		R^2	0.99
	Phase 2	$K_p \{(\text{min}^{(1/2)} * \text{mg})/\text{g}\}$	0.46
		C	179.04
		R^2	0.96
Pseudo-first-order		K_1 (1/min)	0.019
		q_e (mg/g)	4.48
		R^2	0.92
Pseudo-second-order		$K_2 \{(\text{min} * \text{g})/\text{mg}\}$	0.038
		q_e (mg/g)	181.82
		R^2	1
		$h \{ \text{mg}/(\text{g} * \text{min}) \}$	1256.22

It was clear from the outcomes that the process was more closely matched to the IPD and PSO than the PFO. The rate-determining step is shown in Figure 7(b) and is described by the IPD model, which also includes information about the reaction trails. The q_t versus $t^{1/2}$ graph illustrates two linear sections, showing that the adsorption process is multi-step [30]. The R^2 values of the first

phase and second phase are 0.99 and 0.96 respectively. Among the two phases, the first phase rate is higher which is slowing down step by step in the next phase. The R^2 value of PSO is 1 which is higher than the PFO (0.92) [31]. In addition, the q_e value for the PSO equation is 181.82 mg/g, which is close to the test result of q_e (180.61 mg/g). So, it can be assumed that the process rate involves chemical sorption by replacing or sharing valence bond electrons between chromium and RGO [32].

CONCLUSION

This study elucidates the nanoparticle as an excellent adsorbent that can effectively remove chromium (III) ions. The high removal efficiency (90.31%) with significant adsorption capacity and less amount of adsorption time explores its usability as well. Moreover, the kinetic model also provided information about the potentiality of the adsorbent where it followed the pseudo-second-order model more. On the other hand, RGO exhibited a better fit with Langmuir which indicates monolayer adsorption. So, this astounding adsorbent with a large surface may have applicability in future for removing chromium (III) ions from natural and industrial effluents with minimal time.

Author Contributions

All the authors had contributed equally and Chowdhury Manjushree supervised the research. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

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