Research Article

Alternative Composite Nanosorbents Based on Turkish Perlite for the Removal of Cr(VI) from Aqueous Solution

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New nanocomposite sorbents were synthesized and used for Cr(VI) removal from aqueous solution by modifying Turkish perlite with α-MnO$_2$ (PAM) and γ-Fe$_2$O$_3$ (PGI) nanoparticles. Nanocomposite sorbents were characterized using scanning electron microscopy (SEM) and FTIR. The effects of several parameters such as contact time, amount of sorbent, pH, and concentration were investigated and it was found that the sorption capacity for Cr(VI) was found to be highly pH dependent. Also the experimental data were evaluated in terms of different isotherm models. The data of PGI were well fit to DR isotherm model whereas PAM data were well described with Temkin isotherm model. The sorption capacities were found to be 8.64 and 7.6 mg g^{-1} for PGI and PAM, respectively. This confirms that these nanocomposites retain the constituent nanoparticle properties while being macroscopic particles suitable for chromium removal in water treatment.

1. Introduction

Due to rapid technological developments and industrialization especially in developing countries, people both experience a contribution for their comfortable lives and are exposed to important environmental problems [1–4]. Presence of heavy metals in the environment, which are known to have atomic weights higher than 63.5 and specific gravity higher than 5.0, is very important for human beings and living things in terms of their toxicity and carcinogenicity. It becomes a health problem when high concentrations of heavy metals directly or indirectly come in contact with agricultural areas, underground water sources, humans, and animals. All over the world, discharged wastewater of industrial activities includes heavy metals such as copper, nickel, arsenic, chromium, lead, and mercury [5–10].

Among these heavy metals, chromium and its compounds have wide range of uses in industry such as electroplating, leather tanning, metal finishing, nuclear power plant, steel fabrication, photography industries, and textile industries [11–15]. In aqueous solution chromium exists both in trivalent and hexavalent forms, among which the latter one is more toxic and harmful than the other. Trivalent chromium is considered as an essential micronutrient for human, plant,

and animal metabolism whereas hexavalent chromium is extremely mobile in the environment, accumulates in the food chain, and is carcinogenic and mutagenic to living organisms. For total chromium, the maximum allowable drinking water standard is stated as 0.1 milligrams per liter (mg/L) by EPA [12, 16, 17].

Different from organic contaminants, heavy metals especially chromium are not easily removed or biologically degraded. Hence, it is necessary to apply an effective method for its removal from aqueous solutions. Many conventional methods are used for the removal of hexavalent chromium, such as ion exchange, reverse osmosis, and precipitation, which are not preferred because of their high operational and maintenance costs and formation of high amounts of sludge and disposal of it. However, adsorption processes with various adsorbents have been preferred due to their advantages including economy, effectiveness, and efficiency [14–16, 18–20]. Moreover, ease of design and process can be mentioned among the reasons of their preference. Sometimes, the adsorbents used in this process might be regenerated and reused, desorption process may be applied, and it may be advantageous over other processes from this point of view [10, 11, 13, 21, 22].

A wide range of adsorbents have been stated for the removal of hexavalent chromium from aqueous solutions. When these adsorbents are classified as synthetic and natural, activated carbons [5, 6] and resins [17, 19, 23] are respected in the first group whereas agricultural wastes [24], zeolites, clays, rocks, minerals, and industrial wastes can be ranked in the latter one which have been increasingly used due to their abundant existence in nature. Among these naturally occurring materials, perlite with its high silica content is a well-known construction material as well as with limited studies about its high adsorption characteristics for the removal of dyes and heavy metals in the literature. Moreover, nanoparticles due to the advantage of having small particle size and high surface area present attractive and alternative adsorption performance for the removal of heavy metals. This is accomplished by their surface chemistry tailored for ion adsorption. Using these naturally occurring materials as a support material and coating them with nanomaterials having special unique physical and chemical properties improve adsorbents and make them efficiently applicable for adsorption processes when compared to their usual forms. Therefore, for enhancement of adsorption ability of these naturally occurring adsorbents, sometimes they are coated with nanoparticles via coprecipitation method [25] and nanomaterial coated adsorbents are used in less amounts with higher removal efficiency.

Perlite which is a hydrated, glassy rock formed by cooling of volcanic eruptions consists of layers of SiO_2 and Al_2O_3 resulting in a unique structure for various reasons. When applications of perlite are considered, it is mainly consumed as fillers, filter aids, building construction materials [26–28], adsorptive materials for removal of heavy metal ions [29], and other pollutants such as dyes [30]. In this study, perlite which is an industrial mineral was coated with α-MnO_2 and γ-Fe_2O_3 nanoparticles [31] and used for Cr(VI) removal. Characterization of these two nanocomposites was performed and the effects of various parameters on the adsorption process were taken into consideration.

2. Materials and Method

2.1. Materials. All chemicals were of analytical grade and they were used without further purification. The chemicals were obtained from Merck (USA) and nanomaterials were purchased from Sigma (Germany). The expanded perlite, which is a chemically and thermally modified natural perlite and is used as a soil additive, was obtained from Turkish company. Stock solution (1000 mg/L) of Cr(VI) was prepared by dissolving $K_2Cr_2O_7$ (Merck, USA) in deionised water. The Cr(VI) solutions of required concentrations for further experiments were made by diluting the stock and adjusting the pH with HCl or NaOH.

2.2. Synthesis of Nanocomposites. For the synthesis of perlite/γ-Fe_2O_3 composite, 0.5 g of γ-Fe_2O_3 nanoparticles and 1 g of perlite powder were suspended in 30 mL of a water : ethanol (1 : 1, v/v) solution and homogenized in an ultrasonic bath for 6 h. Then, the sample was kept overnight

in a glass flask at room temperature to allow the sample to precipitate. The liquid was removed and the precipitate was dried at 80°C for 12 h. The finally obtained nanocomposite was denoted by PGI.

In addition to this, to synthesize perlite/α-MnO_2 composite, perlite and α-MnO_2 powder blend (2 : 1 w/w) was first gently mixed in a 20 mL water : ethanol (1 : 1, v/v) solution using a glass rod. After that, 10 mL of the solution was placed into each of two grinding jars and ground in an ultrasonic bath at a frequency of 20 Hz for 2 h. The sample was then kept overnight in a flask at room temperature, allowing the particles to precipitate. The liquid part was removed and the precipitate was dried at 80°C for 12 h. The finally obtained nanocomposite was denoted by PAM [25, 31].

All experiments were conducted in a 100 mL bottle placed on a shaker (200 rpm) at room temperature. The pH of the solution was manually maintained at the desired value using 0.1 M HCl and 0.1 M NaOH. The pH was readjusted when necessary by addition of the acid or the base.

2.3. Adsorption Isotherms. In order to optimize the sorption process, the interaction of nanocomposite materials with the heavy metal and the equilibrium data are very important. The relationship between adsorbent and amount of adsorbed material at equilibrium is well described by means of adsorption isotherms. There are many different types of isotherms present in the literature models with one, two, or three parameters. By taking the ratio of adsorbed amount to that remained in the solution at equilibrium into account, the equilibrium relationships between sorbent and sorbate can be presented. Moreover, adsorption isotherms are important in terms of describing the surface area of adsorbent and its porosity.

For the equilibrium evaluation of Cr(VI) adsorption by two nanocomposites, first of all, different concentrations of solutions were prepared from stock solution. Then, the predetermined amount of nanocomposite was mixed with solution having different concentrations of Cr(VI) for optimum contact time. After calculation of adsorbed amount as well as remained amount at the end of optimum period of contact, isotherm models such as Langmuir, Freundlich, D-R, Scatchard, and Temkin were taken into consideration among several isotherm models [32–34]. They are generally based on the ratio between adsorbed amount and the remaining amount in the solution at equilibrium. The linear forms of equations belonging to each isotherm are given in Table 1.

3. Results and Discussion

3.1. Characterization of Sorbents. The characterization related to physical structure of raw perlite and the sorbents obtained from perlite after modification with nanoparticles was carried out both by SEM and FTIR. Figure 1 shows the FTIR results of perlite, PAM, and PGI sorbents with their functional groups. According to the analysis, the observed peak around 1000 cm^{-1} can be attributed to Si–O bonds in three of the sorbents in decreasing vibration order for P, PAM, and PGI, respectively. The absorption less than 850 cm^{-1} corresponds

TABLE 1: Isotherm models and parameters.

Isotherm model	Linear equation	Plot	Parameters		
Langmuir			A_s	K_b	R^2
PGI	$\dfrac{C_e}{q_e} = \dfrac{1}{K_b A_s} + \left(\dfrac{1}{A_s}\right) C_e$	(C_e/q_e) versus C_e	0.0712	238	0.994
PMA			0.0399	272	0.970
Freundlich			k	n	R^2
PGI	$\log q_e = \log k + \dfrac{1}{n} \log C_e$	$\log q_e$ versus $\log C_e$	3.18	0.518	0.987
PMA			13.4	0.491	0.953
DR			X_m	E	R^2
PGI	$\ln q_e = \ln X_m - K\varepsilon^2$	$\ln q_e$ versus ε^2	0.133	8.45	0.996
PMA			0.0745	8.45	0.968
Scatchard			K_s	Q_s	R^2
PGI	$\dfrac{q_e}{C_e} = Q_s K_s - q_e K_s$	q_e/C_e versus q_e	252.7	0.0691	0.973
PMA			206.9	0.0454	0.921
Temkin			B_T	K_T	R^2
PGI	$q_e = B_T \ln K_T + B_T C_e \quad \text{with } B_T = \dfrac{q_m RT}{\Delta Q}$	q_e versus $\ln C_e$	62.74	0.919	0.992
PMA			91.44	0.922	0.972
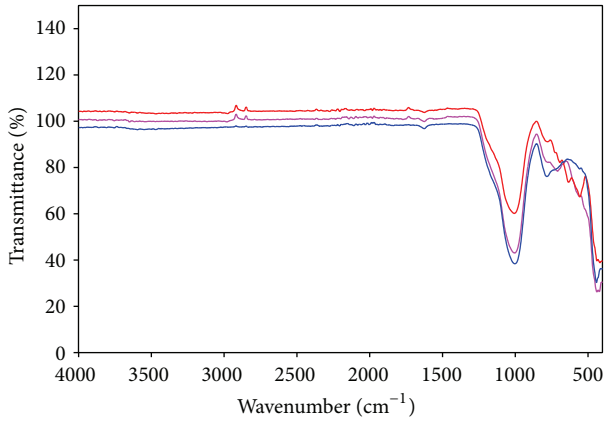
FIGURE 1: FT-IR spectrum of (a) perlite (P) (blue), (b) perlite/α-MnO$_2$ composite (PAM) (pink), and (c) perlite/γ-Fe$_2$O$_3$ composite (PGI) (red).

to Al–O or Si–O–Al vibrations [26–28] which are partially lost for the composites of perlite (Figure 1). Here, it can be specified as the absorption at 795 cm^{-1} corresponds to Si–O–Al vibrations whereas the peak around 630 cm^{-1} corresponds to Al–O vibration. In Figure 2, the scanning electron microscope pictures of the sorbents are given and the changes in the shape of perlite particles can be seen. After coating with nanoparticles, the appearance of perlite in microscale changed into a sorbent whose image can be observed in nanoscale.

3.2. Effect of Adsorbent Dosage. The amount of sorption at any time t, q_t (mg/g), was calculated by a mass balance relationship:

$$q_t = \frac{C_0 - C_t}{w} V, \tag{1}$$

where C_0 and C_t (mg/L) are the liquid-phase concentrations at initial and any time t, respectively, V is the solution volume (L), and w is the amount of nanocomposites (g).

First of all, effect of adsorbent dosage on the removal of Cr(VI) by nanocomposite materials was investigated and the results are indicated in Figures 3(a) and 3(b) for 24 h adsorption process to determine the optimum amount of adsorbent. It can be seen that percentage of Cr(VI) removal increases with an increase in nanocomposite dosages. Specifically, the extent of Cr(VI) removal from 25 mL of 20 mg/L Cr(VI) solution changes from 12.7% at a dose of 0.01 g to 52.5% at a dose 0.10 g of PGI and from 13.9% to 48.0% with the same amounts of PAM. The increase in the amount of the nanocomposites influenced the extent of adsorption due to the increase in the number of sites active for adsorption so it also influenced the removal efficiency of the process. In a similar way, the increase in sorption percentage can be observed with the increase in the amount of commercial resins used for the removal of Cr(VI) [4].

3.3. Effect of Contact Time. The contact time was varied from 5 to 180 min for the adsorption of Cr(VI) by the nanocomposites. The effect of contact time on the adsorption of Cr(VI) is shown in Figures 4(a) and 4(b). The adsorption of Cr(VI) increased with increasing contact time and attained an optimum at about 60 min for both nanocomposite adsorbents. High adsorption rates of chromium for them are observed at the onset, and then plateau values are reached. Therefore, this optimum contact time (60 min) will be used for the following experiments. Also, the sorption percentage in minimum time was higher for PGI than PAM. It is due to different diffusion resistance by these modified adsorbents and because of different binding mechanism indicated by them. Here, for the adsorption of Cr(VI) onto PGI, the ions were bound on the external surface of the adsorbent whereas the binding of hexavalent chromium ions occurs via diffusion through tunnel-like structure of PAM. This is why the sorption percentage of PGI was higher than that of PAM.
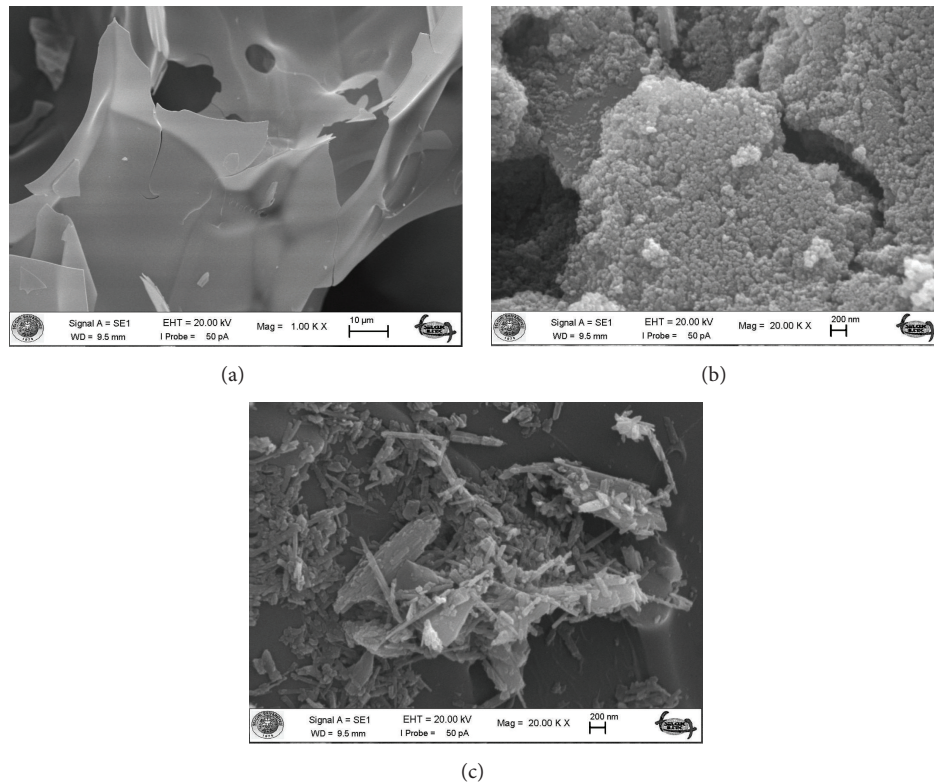
(a)

(b)

(c)

FIGURE 2: SEM images of (a) perlite (P), (b) perlite/α-MnO$_2$ composite (PAM), and (c) perlite/γ-Fe$_2$O$_3$ composite (PGI).
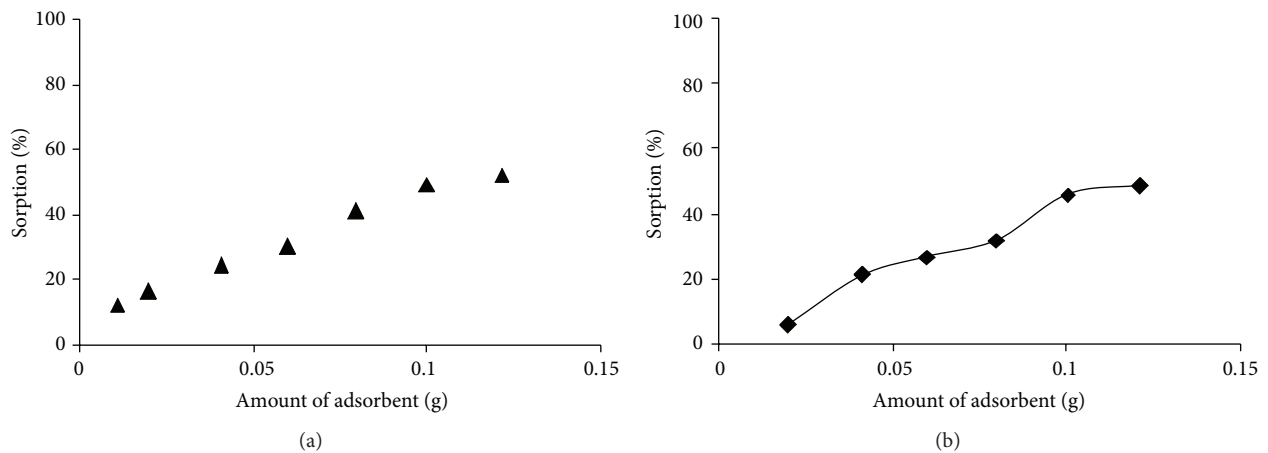

(a)

(b)

FIGURE 3: Effect of adsorbent dosage on the removal of Cr(VI): (a) PGI and (b) PAM.

3.4. Effect of pH. After investigating the effect of contact time on the Cr(VI) adsorption, to find the optimum pH value for the present adsorption process, experiments were performed with different pH values [3–6] (Figure 5).

The effect of pH on the adsorption of Cr(VI) ions by nanocomposite materials was investigated within a range of 1 to about solution pH, that is, 4.4. In order to adjust the pH of the solution, 0.1 M of HCl and NaOH solutions was used. The change in sorption percentage with respect to solution pH is given in Figure 5. The effect of pH on the adsorption process is significantly related to understanding

the interaction, especially electrostatic interaction, between the interface of the solution and the solid. The first and second acidity constants, pKa$_1$ and pKa$_2$, of chromic acid are 0.74 and 6.50, respectively. Moreover, the zero points of charge (ZPC) belonging to γ-Fe$_2$O$_3$ and α-MnO$_2$ which show the variation of the surface charge from positive to negative are 7.1 and 4.8, respectively. Below these points of zero charge, the surface of the adsorbents becomes positive while Cr(VI) species are negatively charged [5–8, 22]. From lower pH values to the value of ZPC, the particle surface becomes positively charged, while Cr(VI) exists predominantly in dianionic (CrO$_4{}^{2-}$) and

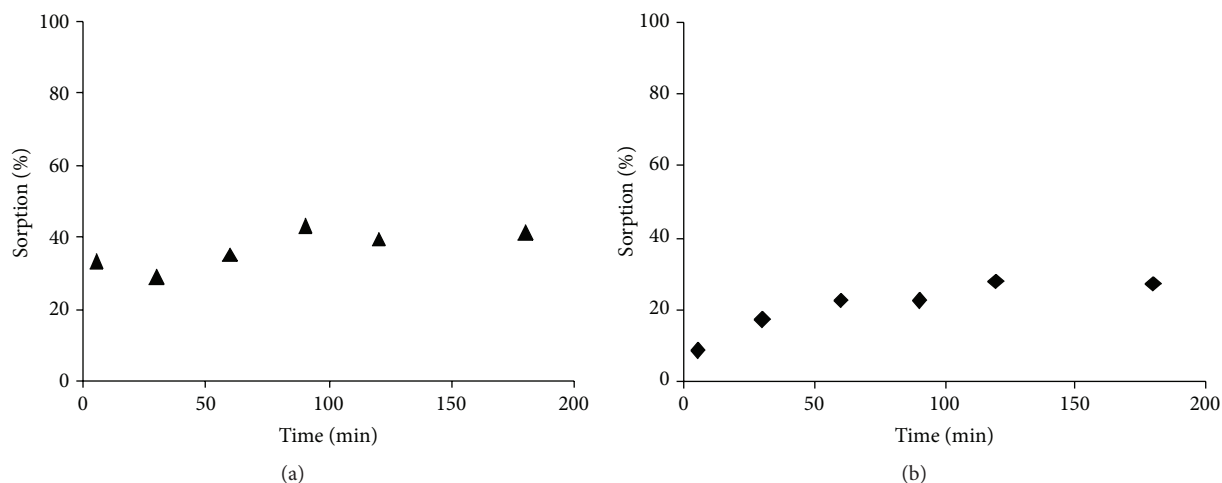FIGURE 4: Effect of time on the removal of Cr(VI) by (a) PGI and (b) PAM.
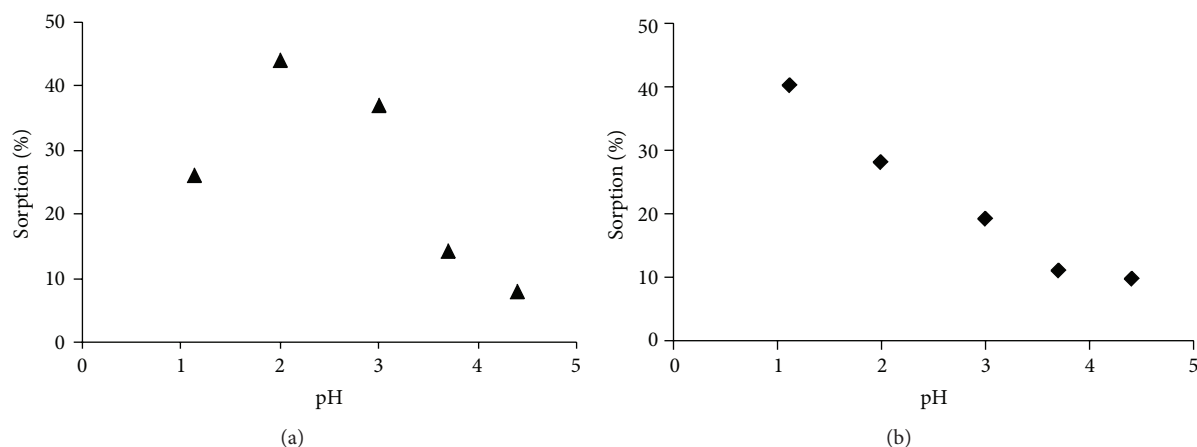

FIGURE 5: Effect of pH for (a) PGI and (b) PAM.

monoanionic ($HCrO_4^-$) forms resulting in a decreased electrostatic attraction, that is, decreased adsorption. Thus, under mildly acidic conditions, attractive electrostatic interactions between negatively charged Cr(VI) species and the positive surface of adsorbent lead to favorable adsorption. This is why we observed that the removal efficiency of Cr(VI) was high at lower values of pH. Similarly, in another study [28] where perlite was used as an adsorbent for the removal of methyl violet, it was stated that surface charge development was important in improved adsorption of the dye with the increase in pH. Above the pH of ZPC, the particle surface processes an overall negative charge while the dominant species of Cr(VI) is CrO_4^{2-} and thus under basic conditions electrostatic repulsion exists and poor adsorption is observed.

3.5. Adsorption Isotherms. The adsorption of Cr(VI) by two nanocomposites was investigated via isotherm models such as Langmuir, Freundlich, D-R, Scatchard, and Temkin. The constants of isotherm models were calculated and the results are given in Table 1 [32, 33]. The correlation coefficient shows the degree of fitting between observed data at equilibrium

and the equations of isotherm models [34]. When correlation coefficients of the models were compared, it was determined that although all models except Scatchard resulted in correlation coefficient higher than 0.99 for PGI, Temkin isotherm model best fitted to the data of PAM.

4. Conclusion

Batch experiments were carried out in order to investigate the removal efficiency of Turkish perlite which is a natural rock coated with commercial nanoparticles such as α-MnO_2 and γ-Fe_2O_3 to remove Cr(VI) from aqueous solutions. The maximum adsorption capacities of PGI and PAM were found as 8.64 and 7.6 mg g^{-1}, respectively. Commercially available nanoparticles with their high specific surface area and adsorption tendency improved the adsorption capacity of Cr(VI) sorption by raw perlite from aqueous solution. Ultrasonic bath was practically applied for the synthesis of these nanocomposites in powder form. Moreover, used magnetic sorbents can be reused. In this study, several isotherm models were taken into consideration in order to describe

the equilibrium data and, as a conclusion, DR and Temkin isotherm models were best fitted to the data of PGI and PAM, respectively. Finally, it can be concluded that nanocomposite sorbents prepared in this study are suitable and efficient adsorbents for the removal of Cr(VI) from aqueous solution. These newly synthesized nanocomposite materials can be applied for the removal of other heavy metals, dyes, and pesticides.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

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