

Evaluation of Cr (VI) Ion Removal from Aqueous Solution by Bio-Inspired Chitosan-Clay Composite: Kinetics and Isotherms

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ARTICLE INFO

Article history:

Received: 2018-07-10

Accepted: 2018-09-22

Keywords:

Chitosan,
Bioinspired Adsorbent,
Bijoypur Clay,
Chromium (VI) Ions,
Adsorption Isotherm,
Adsorption Kinetics

ABSTRACT

This paper reports the evaluation result of adsorbing Cr (VI) ions on sorbent prepared from chitosan (CHT), a versatile derivative of chitin, and dodecyl amine modified locally available kaolinite clay (Bijoypur clay) (MC) that has excellent mechanical properties and great resistance to chemical and biological attack. The effect of the initial metal ion concentration, solution pH, contact time, and adsorbent dosages on the adsorption capacity of the composites was investigated. pH of 4 was selected for better adsorption by the adsorbents. The adsorption abilities were studied over Cr (VI) ions using different adsorption isotherms such as Langmuir, Freundlich, and Dubinin-Radushkevich, respectively. Langmuir isotherm is found better fitted with maximum adsorption capacity of 73 mg/g by composite SB-1. R² obtained from Langmuir isotherm is 0.999, which indicates a monolayer adsorption on the adsorbent surface. The adsorption kinetics was also well described by the pseudo-second-order equation with a rate constant of 0.000302 gmg⁻¹min⁻¹ at 25 ppm Cr (VI) concentration. The adsorption of Cr (VI) ions by the adsorbent was confirmed by FT-IR and X-RD analysis of the composites before and after Cr (VI) ion adsorption. The desorption percentage of the metal ion and the second cycle metal adsorption by the regenerated (regenerated after the first adsorption by fresh adsorbent) adsorbent processed with 0.01N sulphuric acid show values of 78.23 % and 68.12 %, respectively.

1. Introduction

In Bangladesh, industrial wastes are increasing due to rapid industrialization and exponential growth in the demand for industrial products and pollute the environment incorrigibly. Among all the industrial wastes, tannery effluents are

considered to be a major contributor of pollutants to the environment (dos Santos Moyses et al., 2017; Azom et al., 2012). Tannery wastewaters are mainly characterized by high salinity, high organic contaminants, sulfides, and chromium (Akter et al. 2018; Song et al., 2000). Chromium is a potential

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carcinogen that has tertiary effects on humans (Huang et al., 2017b). Chromium exists in two general forms of Cr (III) and Cr (VI) (Alidokht et al., 2011). Trivalent chromium [Cr (III)] at a trace level is an important nutrient for animal metabolism (glucose metabolism, nucleic acid synthesis, etc.) and for plant, too, whereas high levels of chromium (mainly hexavalent chromium, Cr (VI)) are responsible for serious health issues such as skin disease, nausea, and lung cancer. Besides these adverse effects of Cr (Singh et al., 2017) in modern times, various process industries are using chromium (VI) in pigment manufacturing, leather tanning, wood treatment, chrome plating, etc. (Pandey and Mishra 2011).

Among the discrete oxidation states (-2 to +6) of chromium, [Cr (VI)] is considered highly toxic (Singh et al., 2017). This is also considered as a mobile species in aquatic systems, thus exerting carcinogenicity and toxicity on biological systems owing to its strong oxidizing properties.

In contrast, this toxicity of less soluble Cr (III) is lower compared to Cr (IV). Due to its hazardous nature, Cr (VI) must be removed from wastewater prior to discharge into the environment. Among various techniques available, adsorption has been recognized as a popular method due to its simplified operational steps, high efficiency, cost-effectiveness, easy recovery steps, regeneration capacity, and sludge-free operation (Zhang et al., 2016). Therefore, adsorption of Cr (VI) is considered the most economical and effective method to remove chromium from wastewater (Liu and Huang 2011). Many adsorbents have been reported for the detoxification of Cr (VI) contaminated waters, such as polypyrrole/cellulose fiber composites, tannic acid immobilized

powdered activated carbon with humic acid, modified activated carbon, magnetic nanocarbon, zero-valent iron nanoparticles, etc. (Gong et al., 2013; Huang et al., 2017a; Liu et al., 2012; Su et al., 2018; Zhou et al., 2018). However, most of the adsorbents have the weak mechanical strength and low adsorption capacity and are easily susceptible to oxidation and agglomeration. These drawbacks have limited the applications for Cr (VI) removal from wastewater. Therefore, it is necessary to develop new adsorbents with high adsorption capacity and stability for Cr (VI) removal.

Chitosan (CHT) is one of the most important natural polymers composed of layers of crustaceans and cell walls of many fungi. Chitosan is the deacetylated form of chitin, which is a linear polymer of acetyl-amino-D-glucose. Chitosan is hydrophilic, biodegradable in nature, friendly for living things, and easy to perform many chemical derivatizations. Besides, chitosan has many amino and hydroxyl groups that can chelate heavy metal ions. Therefore, chitosan is presented as a very promising starting material for chelating resins (Kandile and Nasr 2009). More specifically, in chitosan molecule, the amino sites are the main reactive groups for metals ions, although hydroxyl groups (especially, in the C3 position) may contribute to the sorption process. Several metals are preferentially adsorbed in acidic media, while chitosan can dissolve in an acid condition (Biswas et al., 2017). To overcome such a problem modification of chitosan or preparation of composite with other materials is an alternative to increase its suitability for the application in all media. Clays and their modified forms have been employed extensively for the removal of chromium

because of the low cost and higher efficiency (Ghnimi and Frini-Srasra 2018) (Leonel et al., 2012). In this study, locally available Bijoypur clay was used, which is rich in kaolinite clay mineral. It consists of a high percentage of SiO₂ (70.08 %), a substantial amount of Al₂O₃ (27.24 %), and fairly low impurity content such as Fe₂O₃ (1.03 %) and TiO₂ (1.65 %) (Mousharraf et al., 2012). Bijoypur clay is a readily available hydrous aluminosilicate containing exchangeable cations and anions on the surfaces that act as active sites for heavy metal adsorption.

Chitosan-Bijoypur clay composites were synthesized to overcome the limitations of chitosan and clay. Unlike montmorillonite clay, kaolinite has 1:1 structure, and there is no substitution of Si⁴⁺ with Al³⁺ in the tetrahedral layer and no substitution of Al³⁺ with other ions (e.g. Mg²⁺, Zn²⁺, Fe²⁺, Ca²⁺, Na⁺ or K⁺) in the octahedral layer. As a result of the presence of broken edges on the clay crystals, kaolinite has a small neat negative charge. This negative charge, although small in quantity, is responsible for the surface which is not completely inert (Bhattacharyya and Gupta 2008). The little charge on clay allows electrostatic interaction with a positively charged ion (possibly metal ion). Moreover, Kaolinite has a relatively low cation-exchange capacity (CEC) of 3–15 meq/100 g of clay and a small surface area ranging from 10–20 m²/g. However, proper modifications can be made to treating its natural state by physical or chemical treatment processes to improve the sorption capacity. It was found that the reactive edge sites of kaolinite could be coated with an adsorbed organic matter to increases its metal ion adsorption capacity (Al-Essa and Khalili 2018). In this study, the raw clay is modified with Dodecyl amine, thus improving its

sorption capacity.

The successful preparation of chitosan-Bijoypur clay composites (film form) at different ratios has been done, and the complete characterization is made in our previous study (Biswas et al., 2017). However, a further modification was performed in its fabrication technique to achieve high kinetic rates of dye and heavy metal adsorption and would be discussed in the experimental section. The composite was characterized to evaluate its suitability as an adsorbent for Cr (VI) removal from aqueous solution. Furthermore, the effect of pH, Cr (VI) ion initial concentration, and the dosages for the removal of Cr (VI) ions respectively in aqueous solution were also investigated. The maximum adsorption capacity of the composite was determined by studying the adsorption isotherm and was compared with different adsorbents obtained in the literature. After Cr adsorption, the composite is desorbed in a separate experiment and regenerated by an appropriate chemical. Removal percentage was compared between the fresh adsorbent and regenerated adsorbent at the end of Section 3.

2. Materials and methods

2.1. Materials

Waste prawn shells were collected from a local prawn hatchery of Satkhira District, Khulna Division, Bangladesh. Chitosan was extracted from this waste prawn shell. The second most important raw material is clay and originated in Bijoypur of Netrokona District, Dhaka Division, Bangladesh. Clay was collected from Bangladesh Insulator and Sanitary Factory Limited (BISF), Dhaka, Bangladesh (after screening through 150 mesh screens followed by 200 mesh screens). Sodium hydroxide (Loba Chemie Pvt. Ltd.

India), hydrochloric acid, potassium dichromate, sulphuric acid (E. Merck, Germany), dodecylamine (Sigma-Aldrich, Sweden), and acetic acid (E. Merck, Germany) were purchased for chitosan (CHT) preparation, clay modification, composite fabrication, and adsorption studies.

2.2. Extraction of chitosan and modification of Bijoypur clay

Chitosan (CHT) was extracted from waste prawn shell using our previously reported method (Rahman et al., Rahman et al., 2013; Rashid et al.). The extraction of chitosan from waste prawn shell involved three major steps: (a) deproteinization, (b) demineralization, and (c) deacetylation. The degree of deacetylation (DD) of chitosan was found to be 77.2 %, and the viscosity-average molecular weight of chitosan was determined using a viscometric method through the Mark-Houwink equation. The intrinsic viscosity and molecular weight of chitosan are 144.8 mLg^{-1} and 187128 Da, respectively. The raw clay (RC) was purified by treating with hydrochloric acid. After acid treatment, the purified clay was modified with the dodecyl amine to induce its organophilic character according to the method reported by Yano et al. and was named as a modified clay in this article (MC)(Yano et al. 1993).

2.3. Preparation of chitosan-modified clay composite

The composite of chitosan-clay (CHT-MC) fabricated with a slight modification of the method as reported by Wang et al. (Wang et al., 2005). In a typical procedure, 1 % Chitosan solution and 1 % modified clay dispersion were mixed in different weight ratios and stirred for 4 h at 60 °C. The modified clay amount ranged from 0.33 to 1.5 g. The final mixture was transformed into the particle form by adding the droplets of this

mixture in a solution of 15 % sodium hydroxide and 95 % ethanol.

However, the final mixture can be transformed into a film form and was discussed in our previous study (Biswas et al., 2017). When the final mixture was cast on a petri dish at 60 °C for 48 h in an oven, a film was formed. The dry film still contained a small quantity of the solvent, which formed chitosonium acetate. After drying, the film was soaked in 1M aqueous NaOH solution for 5 h to neutralize the acid followed by rinsing with distilled water and was, then, dried at 60 °C for 24 h.

The composites were prepared with different weight ratios of chitosan and clay, as shown in Table 1.

Table 1

Different weight ratios of chitosan (CHT) and modified Bijoypur clay (MC) in different composites.

Composites	Sample	CHT (wt %)	MC (wt %)
CHT- MC	SB-1	1.50	0.33
CHT- MC	SB-3	0.50	0.50
CHT- MC	SB-5	0.33	1.50

2.4. Characterization

Fourier transform infrared (FT-IR) spectra analysis of pure composite and Cr rich composite were observed on an FT-IR 8400S spectrophotometer (Shimadzu Corporation, Japan). XRD analysis (model BRUKER AXS Diffractometer D8, Germany) (Thermoscientific ARL Quant'x EDXRF Analyzer) of CHT, composite (before and after Cr adsorption), and SEM of the composite in the particle form (JSM-6490) are analyzed. Thermogravimetric analysis with respect to EDXRF of the composites was studied in our previous study (Biswas et al., 2017).

2.5. Batch adsorption experiments

Stock solution of 1000 ppm of standardized chromium Cr (VI) was prepared in distilled-deionized water. Kinetic batch experiments for the reduction of Cr (VI) in water were carried out in polytetrafluoroethylene (PTFE)-sealed bottles covered with aluminum foil at atmospheric pressure. To each bottle, 25 ppm of Cr (VI) solution (prepared with deionized water) and a certain amount of composites were added. The initial pH was adjusted prior to the experiment. All bottles were shaken on a shaker (model: SSL2, Stuart, UK), followed by filtration using Whatman filter paper (0.45 mm). The remaining metal ions in the filtrate were analyzed by UV-vis spectrophotometer (Shimadzu 1700 UV) at 540 nm. Different parameters for Cr (VI) adsorption were studied including the effect of initial metal ion concentration (20-60 mg/L), the adsorbent amount (20-150 mg), agitation time (30-180 min), and pH of adsorbate solution (2-8). The percent removal and amount of metal ion adsorption per unit mass of the composite in equilibrium (q_e mg g⁻¹) were evaluated using the following mass balance equations:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where q_e is the amount of the Chromium adsorbed (mg/g) on the adsorbent, C_0 is the initial concentration of Cr (VI) (mgL⁻¹), C_e is the equilibrium concentration of Cr (VI) in solution (mgL⁻¹), V is the volume of the solution used (L), and W is the weight of the adsorbent used (in gram).

2.6. Batch desorption experiment

The adsorbent recovered after batch equilibrium studies was carefully rinsed with distilled water to remove residual particles and, then, dried. The dried adsorbent (0.01 g) was placed in a stripping solution contained

in 100 mL Erlenmeyer flask. The solution was 25 mL distilled water adjusted to pH of 4 using 0.1 M HCl at 25 °C. Desorption ratio was calculated by Equation 8, as provided in Section 3.6.

For calculating adsorption percentages of the regenerated adsorbent (after the first cycle of using), it is necessary to compare the result with the adsorption observed in the case of the pure adsorbent. For this reason, the experimental condition was kept, as mentioned in Section 2.5 for both fresh and regenerated adsorbents. In the case of used adsorbent, it was regenerated by 0.01 N sulphuric acid; after that, it is dried and used for the second cycle of adsorption. Both of the adsorption percentages were calculated by Equation 9, mentioned in Section 3.6.

3. Results and discussion

3.1. Adsorption studies

3.1.1. Effect of pH

The pH value of the medium is a significant factor in the adsorption process of Cr (VI) over the adsorbent. The pH of the solution varied from 2-8 and kept the other parameters, such as chromium concentration (25 ppm), adsorbent dose (10 mg), and agitation time (120 min), constant. The adsorption results are presented in Fig. 1. The results indicated that the maximum adsorption was achieved at pH of 4 ± 0.1 . At low pH, the active sites of the composites (-NH₂, -OH, -COOH) became positively charged. The adsorption capacity decreased with the increase of the solution pH. It is common that Cr (VI) exists as HCrO₄⁴⁻ and Cr₂O₇²⁻ in solution at optimum sorption pH. In acidic media, HCrO₄⁴⁻ is the dominant resulting from the hydrolysis of dichromate ion, and the increase of pH would facilitate the formation of Cr₂O₇²⁻ from HCrO₄⁴⁻ (Li et al., 2011).

Hence, Cr (VI) is adsorbed on the protonated active sites of the composite. With an increase in the pH (above 4) of the solution, the surface of the adsorbent became negatively charged that resulted in the repulsion of the

chromate ions and the decrease of the adsorption of Cr (VI). The result showed the composite prepared from 2:1 CHT/MC (SB-1) showed the maximum adsorption.

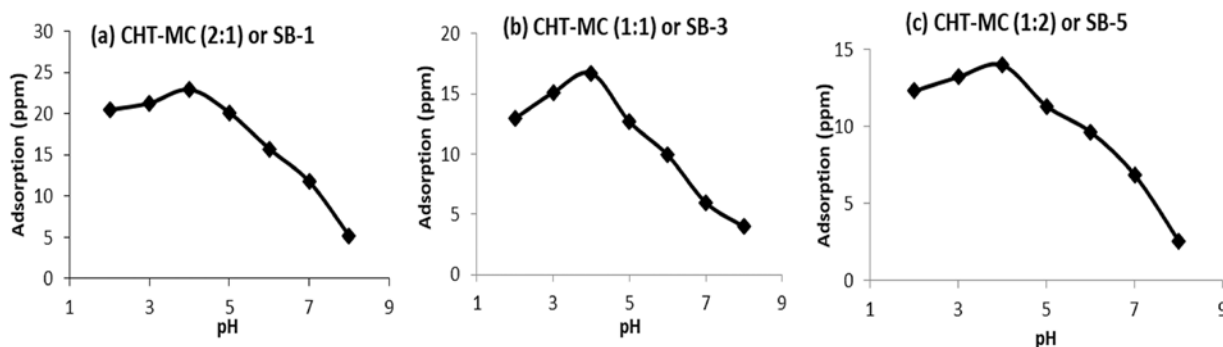


Figure 1. Effect of pH on the Cr (VI) adsorption on the composites.

3.1.2. Effect of Cr (VI) ion concentration

The effect of the initial Cr (VI) concentration on the adsorption is shown in Fig. 2. The effect of Cr (VI) study was investigated by varying the initial concentration from 20 to 60 ppm and keeping all the other parameters constant such as pH of 4, 10 mg of adsorbent dose, experiment temperature of 30 °C, and 2 h of contact time. According to the figure, SB-1 (CHT-MC (2:1)) showed higher

adsorption than the other two composites. The increase of adsorption capacity by increasing Cr (VI) concentration may be due to the utilization of all the active sites from a large number of the amino group derived from the higher ratio of chitosan. On the other hand, CHT-MC (1:2) showed the lowest adsorption due to the small portion of chitosan used in the composite fabrication.

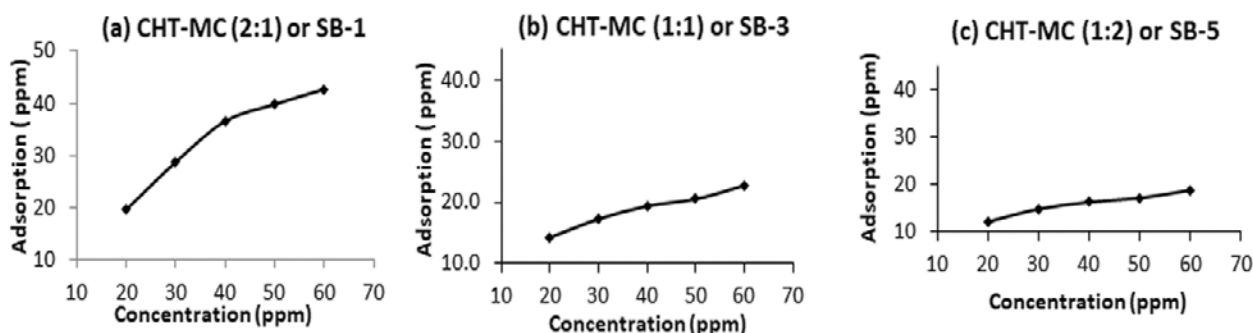


Figure 2. Effect of solution concentration on the Cr (VI) adsorption.

3.1.3. Effect of adsorbent dose

The effect of adsorbent dosage on the removal of Cr (VI) was conducted by varying the number of adsorbents from 10 to 150 mg, while other parameters (such as pH of 4), Cr (VI) concentration (25 ppm), temperature (30 °C), and contact time (120 minutes) were kept

constant, as shown in Fig. 3. It is obvious that the removal percentage of Cr (VI) increased with the increase of adsorbent dosage. However, it is noteworthy to mention that the effect of adsorbent doses on composite SB-1 containing CHT: MC (2:1) is less prominent. The case of SB-1 yielded similar adsorption

by 150 mg for SB-3 and SB-5, respectively, using 10 mg adsorbent. In addition, this result supported earlier observations as the composites with the higher amount of CHT exhibited better adsorption due to a large

number of active sites. Higher adsorbent dosage may lead to particles aggregation, resulting in decreasing the exposed surface area as well as increasing the diffusion path.

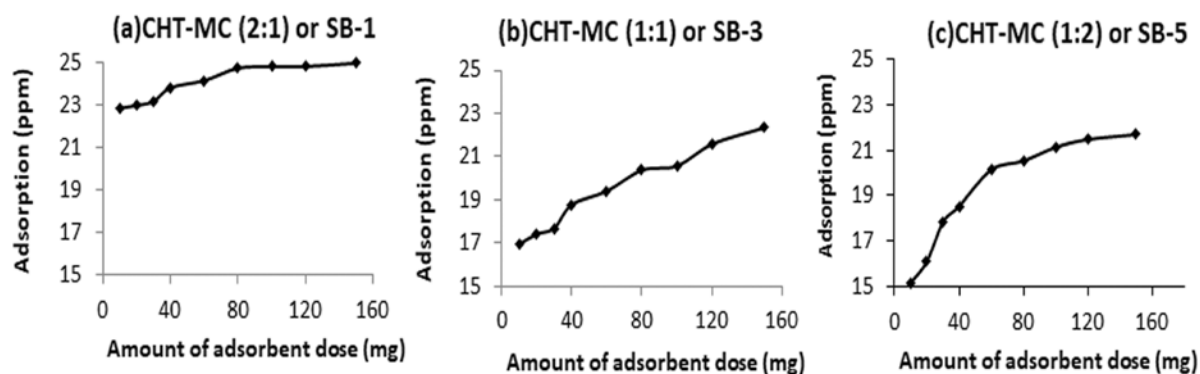


Figure 3. Effect of adsorbent doses on Cr (VI) adsorption.

The data provided in Sections 3.1.1, 3.1.2, and 3.1.3 confirm the equilibrium condition. The maximum adsorption was observed at pH of 4. Above or below this pH, the adsorption data showed a decreasing phenomenon in the amount of Cr (VI) adsorbed. The effect of adsorption dose upon increasing the adsorption dose from 10 mg to 150 mg indicates that the adsorbed amount for SB-1 does not vary so much. SB-5 showed a similar kind of trend above 80 mg of adsorbent. In addition, the effect of concentration showed an increase in adsorption up to a certain point and, then, became visibly constant. However, the best adsorption was found in the case of SB-1

composite. Considering these three changes in the condition, SB-1 performed the best, and a time Vs adsorption (ppm) was investigated separately for SB-1 composite, keeping other conditions constant. This data are provided in Fig. 4. The graph revealed that the amount of adsorbed material remained almost constant above 100 minutes of the time. Moreover, after 180 minutes, a slightly decreasing trend is observed, representing that a time limit for 120 minutes would be optimum for this study. Therefore, above all, the equilibrium condition is set at pH of 4, contact time of 120 minutes or 2 h, an adsorbent dose of 10 mg, and the initial concentration of 25 ppm.

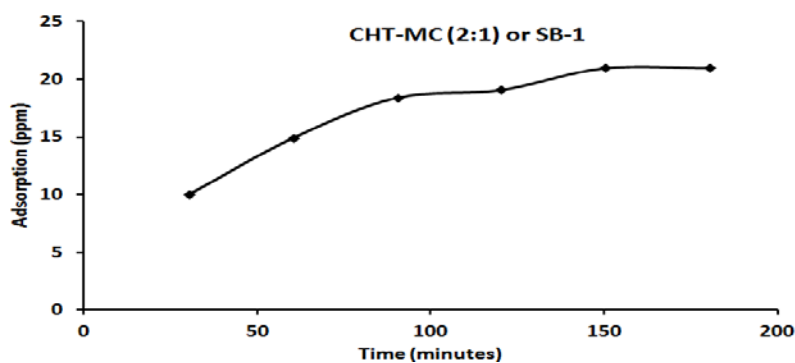


Figure 4. Effect of adsorption time on the adsorption of Cr(VI) by SB-1.

3.2. Adsorption isotherm studies

Adsorption isotherm analysis was performed in order to assess the sorption behavior of the metal ions. Generally, the binding of metal ions to biosorbents often fits with the Langmuir and Freundlich models. Another model, e.g., Dubinin-Radushkevich (D-R), was also employed to discuss the sorption equilibrium of Cr (VI). Cr (VI) solutions of different concentrations at pH of 4.0 were taken for the isothermal studies for all three composites in this study. Herein, 0.01 g of each composite was taken for the adsorption and the mixture was shaken in a reciprocating shaker for 2 h for equilibrium. The equilibrium isotherm model is used to describe the interactions between the adsorbate and adsorbent. The adsorption of Cr (VI) onto CHT-MC composite was studied using Langmuir and Freundlich isotherms. The Langmuir adsorption isotherm is based on a monolayer surface coverage of Cr (VI)

ions on the composite that contains a finite number of adsorption sites of uniform adsorption energies, whereas the Freundlich isotherm was utilized to understand adsorption on heterogeneous surfaces and multiple adsorption layers (Nair et al., 2014). The linearized form of the Langmuir equation can be expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (2)$$

where q_e (mg/g) is the amount of heavy metal adsorbed per unit mass of CHT-MC composites, C_e (mg/L) is the concentration of the remaining heavy metal in the solution in equilibrium, q_m is the maximum amount of heavy metal adsorbed per unit mass of adsorbent, and b is the Langmuir constant. The values of b and q_m were calculated from the slope and intercept of Equation 1 (as shown in Fig. 5).

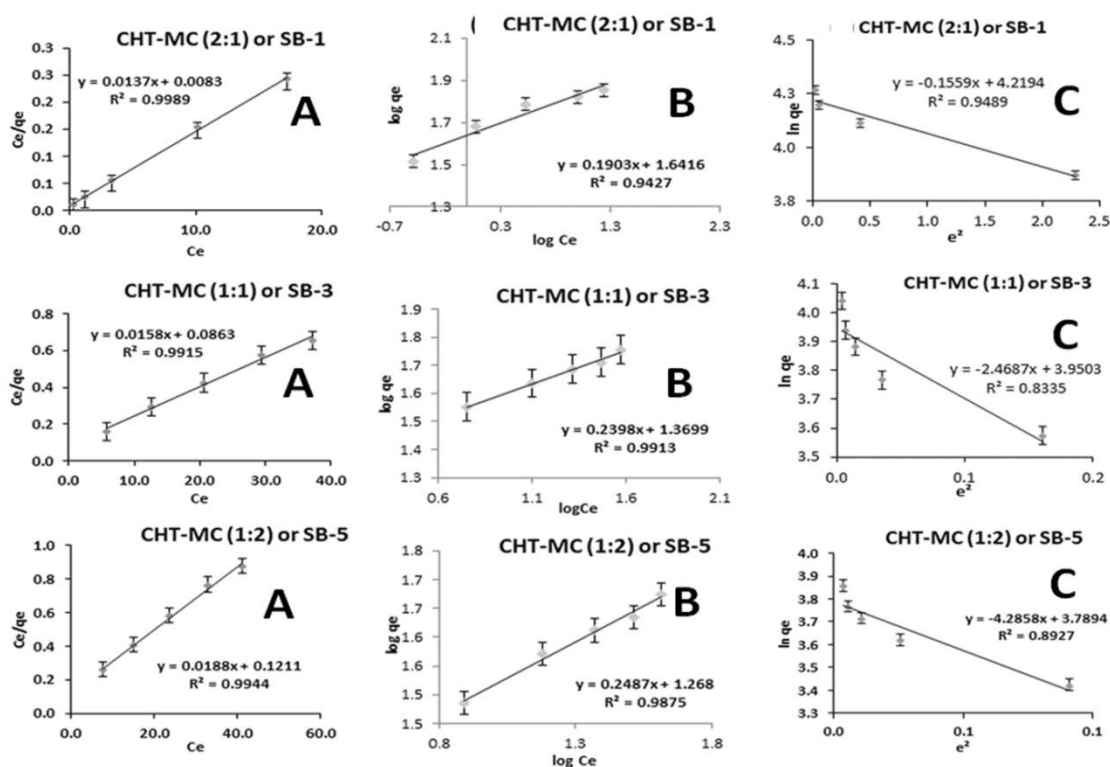


Figure 5. Adsorption isotherm (A- Langmuir isotherm, B- Freundlich isotherm, and C- Dubinin-Radushkevich) of different composites.

Dimensionless adsorption intensity R_L is used to determine the favorability of Langmuir isotherm and is calculated using the following equation (Ozdemir et al., 2004):

$$R_L = \frac{1}{1 + bC_0} \quad (3)$$

where C_0 is the maximum initial concentration of the heavy metal ion. The shape of the isotherm can be identified on the basis of R_L , that is, the isotherm can be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L =$

0). R_L of 0.01-0.09 (as shown in Table 2) suggested that the adsorption of Cr (VI) on the surface of the composites was favorable. Regression coefficients (R^2) of all composites were less than 0.99, showing that those adsorbents favor Langmuir isotherm. Table 2 lists q_m , b , and R_L values of the isotherm of adsorbents for the chromium solution. The highest adsorption 73 mg/g was obtained for CHT: MC-2:1 composite and it decreased with the increase of MC contents in the composites.

Table 2

Thermodynamic parameters for the adsorption of Cr (VI) on chitosan-clay composites.

Sorbents	Langmuir				Freundlich			Dubinin-Radushkevich		
	q_m	b	R^2	R_L	n	K	R^2	β	E (kJ mol ⁻¹)	R^2
CHT:MC(2:1)	73.00	1.65	0.999	0.01	5.26	43.81	0.93	0.16	1.79	0.87
CHT:MC(1:1)	63.30	0.18	0.996	0.08	4.17	23.44	0.99	2.47	0.45	0.83
CHT:MC (1:2)	53.20	0.16	0.994	0.09	4.02	18.53	0.98	4.29	0.34	0.86
Maximum sorption capacity	73 mg/g				43.81 mg/g			67.9925 mg/g		

Freundlich isotherm (Zubieta et al., 2008) is used to identify the non-ideal adsorption of heterogeneous surface energy systems and is expressed as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

$1/n$ corresponds to the order of the isotherm and is considered as irreversible ($1/n = 0$), favorable ($0 < 1/n < 1$), and unfavorable ($1/n > 1$) (Greluk and Hubicki 2010). The value of b 1.65 was obtained for CHT:MC (2:1), which indicates the favorable nature and heterogeneity of the adsorbent sites (Baocheng et al., 2008). The experimental data of Cr (VI) adsorption fitted well with both isotherm models, as shown in Fig. 5. In Equation 4, K_F (mg/g) is roughly an indicator of the adsorption capacity, and $1/n$ is the adsorption intensity. The plots are linear with

a regression coefficient greater than 0.92. The Freundlich constant n (Fig. 5) lies between 1 and 10 for a favorable adsorption process, and a larger value of n implies the effective interaction between the adsorbent and the adsorbate (Febrianto et al., 2009).

The Dubinin-Radushkevich isotherm (D-R) (Chatterjee et al., 2009) is analogous to the Langmuir isotherm; however, it does not assume a homogeneous surface or a steady adsorption potential. The D-R isotherm helps calculate the adsorption energy and the nature of the adsorption mechanism involved in the interaction between chromium and the adsorbent surface (Fig 5, C). The linearized D-R isotherm equation can be written as follows:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (5)$$

where q_e is the amount of Cr (VI) adsorbed in

equilibrium per unit weight of adsorbent (mg/g), q_m is the maximum adsorption capacity, β is a constant related to the adsorption energy, and ε is the Polanyi potential that can be expressed as:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (6)$$

where R is the gas constant ($\text{J mol}^{-1}\text{K}^{-1}$), C_e is the equilibrium concentration of chromium (mg L^{-1}), and T is the temperature (Kelvin). The values of β and q_m were obtained from the slope and intercept of the plot of $\ln q_e$ versus ε^2 .

The regression coefficient values for the composites were found greater than 0.83 (Table 2), representing a good fit for the isotherm (Chen 2015; Dada et al., 2012). The adsorption energy E was calculated by $(2\beta)^{0.5}$. The value of E (<8 kJ/mol) (Jain et al., 2009) (positive in this case) suggested that adsorption process was endothermic, and range of values proved that the adsorption process was associated with physical adsorption, demonstrating the electrostatic attraction between the dichromate ion and composites.

3.3. Kinetic studies

The kinetics of adsorption of Cr (VI) on the composite was evaluated by kinetic models that provided insights into the mechanism and the rate-limiting steps involved, i.e., whether the adsorption is mass transfer controlled or

reaction controlled. The most commonly used kinetic models for studying solid-liquid interactions are pseudo-first-order and pseudo-second-order models based on adsorption capacity. In the pseudo-first-order kinetic model, the adsorption is controlled by diffusion and mass transfer of the adsorbate to the adsorption site. On the other hand, in the pseudo-second-order kinetic model, chemisorption is the rate-limiting step. The adsorption kinetics of Cr (VI) on CHT-MC composite was evaluated using pseudo-first-order and pseudo-second-order models. The rate equations are given as follows (Annadurai et al., 2008):

$$\log(q_e - qt) = \log q_e - k_1 t / 2.303 \quad (7)$$

$$t/qt = 1/k_2 q_e^2 + t/q_e \quad (8)$$

The models relate to the amount of the metal ion adsorbed in equilibrium and at various time intervals to kinetic rate constants k_1 and k_2 . The kinetic parameters (as given in Table 3) are obtained from the respective plots (as shown in Fig. 6) giving the kinetic parameters.

The higher regression coefficient was obtained with the second order kinetics. This indicates that the experimental data show a good fit to this model. The experimental and calculated equilibrium adsorption capacity (q_e) values were found to be 73 mg/g and 68.02 mg/g, respectively, in accordance with the second-order kinetics.

Table 3

Kinetic and intraparticle rate constant data for the adsorption of Cr (VI).

Composite	Second-order rate constant (k_2) ($\text{gmg}^{-1}\text{min}^{-1}$)	Regression coefficient (R^2) (second order)	First-order rate constant (k_1) (min^{-1})	Regression coefficient (R^2) (first order)
SB-1	0.000302	0.9946	0.046060	0.761900
SB-3	0.000596	0.9920	0.047902	0.047902
SB-5	0.000610	0.9970	0.023030	0.961000

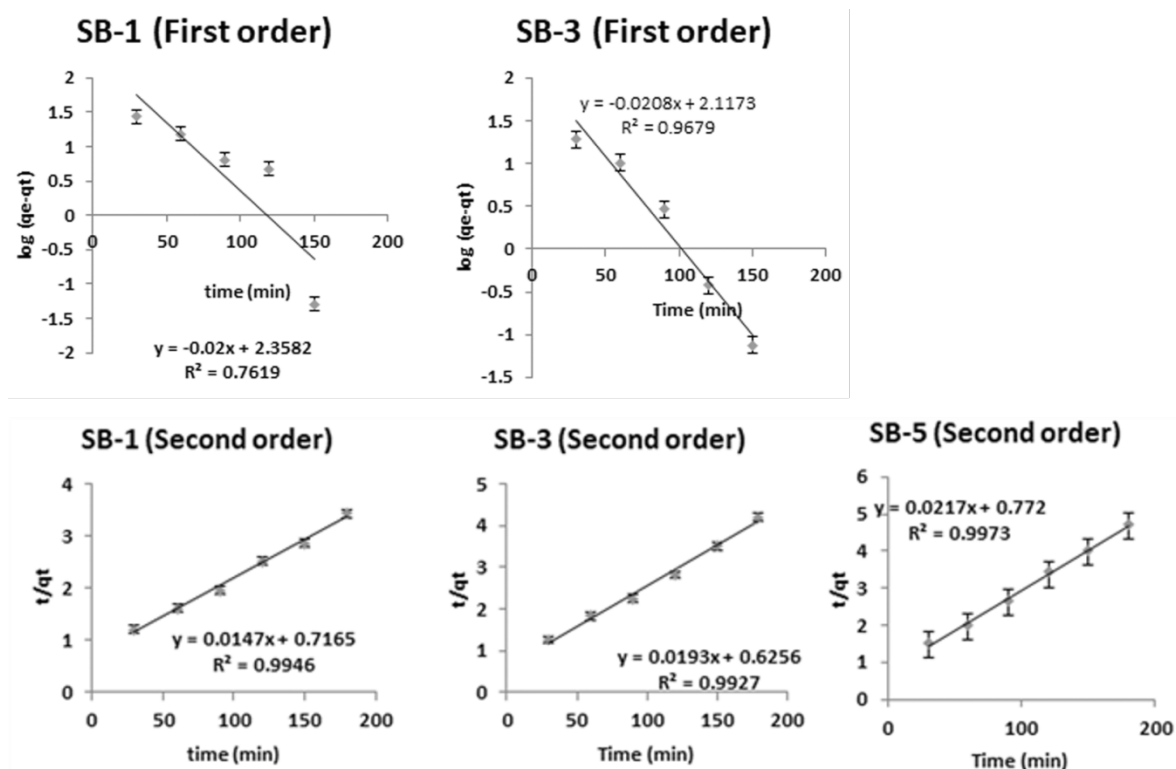


Figure 6. Kinetic plot of Cr (VI) adsorption on chitosan-modified clay composite adsorbent (SB-1, 3 and 5).

Based on the kinetic study and different isotherm studies, a mechanism of chromium adsorption is proposed in this study. A combination of organically modified clay (MC) and chitosan enables two major sites for adsorption. One is associated with $-NH_2$ and $-OH$ groups of the chitosan present on the surface of the composite, and the second one is associated with $-OH$ group on clay. Besides, the clay modifying agent results from some nitrogen atom on the composite surface. The adsorption medium is acidic in nature (pH of 4), which enables amine group to be converted into $-NH_3^+$ group and, at the same time, the nitrogen atom from the clay modifying agent, in some places, is converted to possible positive ions.

Dichromate ion ($Cr_2O_7^{2-}$) and $HCrO_4^-$ are the predominant species in the acidic aqueous solution (Anah and Astrini 2017) (approximately $pH \leq 4$) of chromium. These particles are attracted directly to the positive

sites of the composite by the electrostatic force of attraction. As the mechanism is based on the physical adsorption, easy desorption process can be applied with a considerable recovery of chromium and regeneration of the composite by desired reagents. Chromium is added in the form of potassium dichromate, and it provides a positive charge on the chromium atom in the solution. Thus, a coordination bond is developed between the water molecules and positively charged chromium ion. Since the chromium is positively charged, the orientation of the oxygen atom (negatively charged) of the water molecule will be positioned towards the inward direction, whereas hydrogen atom will be placed in the outward direction, giving a positive periphery. Now, this form of the chromium will be attached to the $-OH$ group above the surface of the composite, providing a possible physical adsorption (Pandey and Mishra 2011).

3.4. Characterization of the composites before and after Cr (VI) adsorption

3.4.1. XRD analysis

The XRD of the composite SB-1 (CHT: MC= 2/1) and Cr (VI) adsorbed SB-1 is shown in Figure 7. As discussed in our previous report (Biswas et al., 2017), the characteristic peak of kaolinite at 40° disappeared in SB-1 in the composite. Moreover, the peak of 22° was broadened and shifted slightly towards a lower angle point. The broadening of the peak of the composite at 20° was also observed with higher intensity than the MC due to the

presence of the CHT in the composite. By comparing SB-1 with Cr (VI) rich adsorbent, the sharpness of the peak of SB-1 at 20° disappeared after Cr adsorption. In addition, the intensity of other peaks either significantly decreased or disappeared after Cr(VI) adsorption, showing the attachment of Cr(VI) to the composite surface clearly. Furthermore, the characteristic peak of kaolinite mineral at 22° has disappeared and, thereby, given rise to a broad shoulder at the same position for the Cr (VI) adsorbed composite.

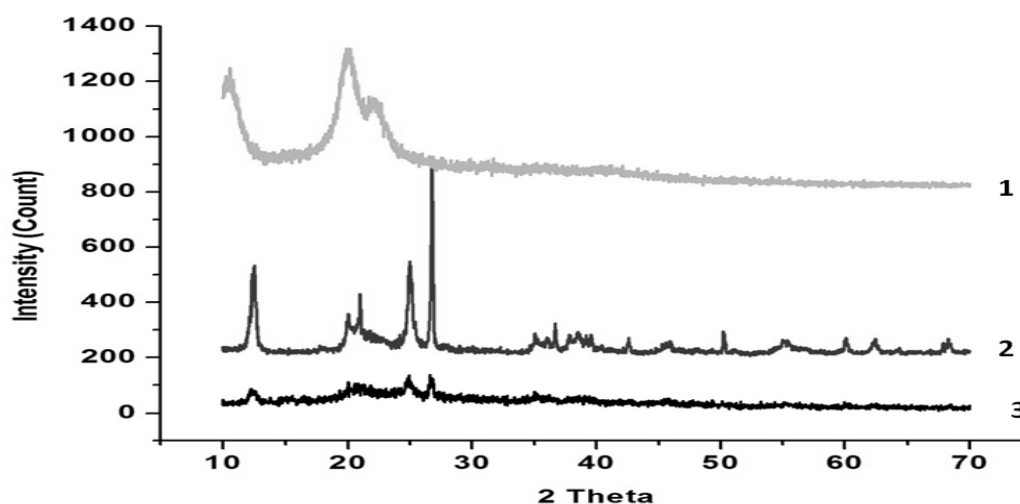


Figure 7. Comparison of XRD for (1) Chitosan, (2) composite SB-1, and (3) SB-1 after Cr (VI) adsorption.

3.4.2. FT-IR analysis

FT-IR spectra of SB-1 and Cr (VI)-adsorbed composite SB-1 were analyzed to confirm the adsorption of Cr (VI) on the possible active sites of the composite. It is evident from Fig. 8 that Cr (VI) adsorbed composites exhibit shifts in the peaks at 3477 to 3444 cm^{-1} . This might occur due to the physical forces involved (electrostatic adsorption) between the adsorbent and adsorbate (Karthik and Meenakshi 2014). A medium intensity band obtained at $1600\text{--}1700\text{ cm}^{-1}$ represented carbonyl (C=O) stretching, where a slight change in the frequency of peaks confirms the

existence of the adsorption. Moreover, intensity of C–O stretching vibrations at 1040 cm^{-1} which reduced after Cr (VI) adsorption further confirmed the binding onto the SB-1 composite. However, in our previous study (Biswas et al., 2017), the presence of the major functional groups in the composites was investigated, and it was found that both chitosan and modified clay were combined successfully in the newly fabricated form. These functional groups are considered as the possible sites for chromium adsorption from aqueous solution.

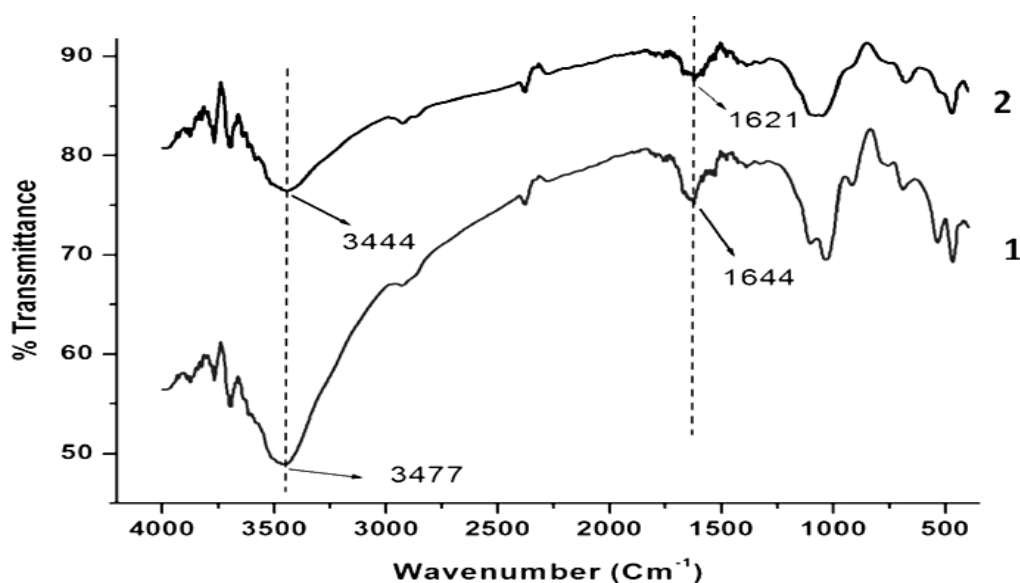


Figure 8. Comparison of FT-IR for (1) composite SB-1 and (2) SB-1 after Cr (VI) adsorption.

3.4.3. Morphological characterization of SB1 composite

The surface morphology of composite SB1 (in the particle form) was investigated by scanning electron micrographs (SEM). At various magnifications, the SEM images of SB1 are shown in Figure 9. SEM micrographs

of the adsorbent at different magnifications showed rough surface morphology (Tirtom et al. 2012), indicating heterogeneity and, thus, providing better adsorption sites. Variable roughness and broken edges on the border were found on the surface of the composite.

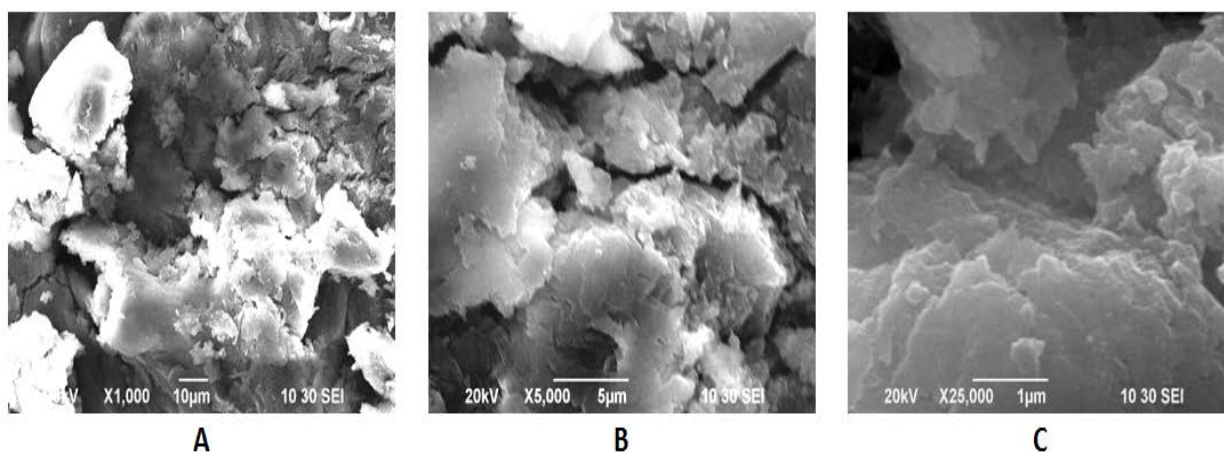


Figure 9. SEM images of composite SB-1 (A) at $\times 1000$, (B) at $\times 5000$, and (C) at $\times 25000$ magnification.

3.5. Comparative analysis

An ensemble of the above investigation suggested that chitosan-modified clay composite (CHT-MC) was a promising material for the adsorption of Cr (VI) ions. The results of the present study were

compared with some other bioadsorbents as reported in the literature, as given in Table 4. The sorption capacity of CHT-MC (2:1) yielded a significantly higher adsorption of Cr (VI) ions from aqueous solutions (as obtained from Table 4).

Table 4

Comparison of the adsorption capacity of different composites similar to the composite developed in the present study.

Material	Maximum adsorption capacity (mg/g)	pH	References
Saw dust	41.50	1.0	(Gupta and Babu 2009)
Activated Carbon (from Fox nutshell)	43.45	2.0	(Kumar and Jena 2017)
Metal ion imprinted chitosan	51.0	5.5	(Tianwei et al., 2001)
Wheat biochar	21.30	2.0	(Wang et al.; Wang et al., 2010)
Silica-based adsorbent	68.0	3.5	(Qiu et al., 2009)
Cross-linked chitosan	50.0	5.0	(Schmuhl et al., 2001)
Chitosan-modified Bijoypur clay biocomposite (CHT-MC)	73	4.0	Present study

3.6. Desorption studies

Percentage of the desorption ratio and adsorption percentages were calculated

according to the following equations:

$$\text{Desorption ratio} = \frac{\text{Amount of metal ion desorbed}}{\text{amount of metal ion adsorbed}} \times 100 \quad (9)$$

$$\text{Adsorption percentage} = \left(\frac{\text{Amount of metal ion after adsorption}}{\text{amount of metal ion in the initial solution}} \right) \times 100 \quad (10)$$

Table 5

Percentages of desorption of chromium (VI) by SB1 composite.

Desorption solution	Composite title	Cr (VI)
0.1 N HCl	SB1	78.23 %

Adsorbed Cr could be stripped by the introduction of protons that competed with metal ions for binding sites in composites. After the first desorption cycle, the composite particle was dried and run for the second step for adsorption of chromium (VI), showing lower adsorption percentage (68.12 %) as compared to the unused pure SB1 composite (88.48 %) (from Equation 10). However, multiple cycles of reusing the composite can provide a better understanding of the economic feasibility of this material.

4. Conclusions

In the current work, we evaluated the

adsorption pattern of novel chitosan-modified clay composites at various combinations. The composite (SB-1) with a ratio of 2:1 (chitosan (CHT): dodecyl amine modified clay (MC)) exhibited maximum adsorption of Cr (VI) compared to chitosan, and many other adsorbents were reported in the previous studies. While analyzing the isotherms, it was found that adsorption of Cr (VI) followed Langmuir isotherm model with a maximum adsorption capacity of 73 mg g^{-1} , and pseudo-second-order kinetic model matched well with the experimental data of Cr (VI) adsorption onto the composite SB-1. Dubinin-Radushkevich isotherm revealed the

endothermic nature of the adsorption process by finding the E value within the range. It was also suggested that a possible mechanism followed by the adsorption could be physisorption. Moreover, from the kinetic study, the highest regression coefficient was observed for second-order kinetic study as compared to the first order. This kind of behavior implies that the adsorption followed the second-order kinetics with calculated q_e of 68.1 mg g^{-1} for SB-1, which is much closer to the experimental value (73 mg g^{-1}) found from Langmuir isotherm. In the end, a considerable desorption ratio was observed showing a value of 78.23 %. In a nutshell, this material could be a possible alternative for Cr (VI) removal from aqueous solution, and further detailed studies of this adsorbent could result in a better agent for removing chromium from the real effluent.

Acknowledgement

The author highly acknowledges the partial grant provided by the Organization for the Prohibition of Chemical Weapons (OPCW) (Project Account No: L/ICA/ICB/194479/14) to carry out the research.

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