



Original paper

A kinetic and thermodynamic study of methylene blue removal from aqueous solution by modified montmorillonite

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ABSTRACT

In current study, sulfonic acid-functionalized ordered nanoporous Na⁺-Montmorillonite (SANM) has been utilized as the adsorbent for the removal of a cationic dye, methylene blue (MB), from aqueous solution using the batch adsorption technique under different conditions such as temperature, adsorbent dosage, initial dye concentration, contact time, and pH solution. The optimum sorption conditions were found as following: contact time 10 min, initial dye concentration 800 mg/L, adsorbent dose 0.3 g and temperature 25 °C. The results indicate that the process is pH independent. The sorption capacity was 500 mg/g for this dye. Different thermodynamic parameters i.e., changes in standard free energy, enthalpy, and entropy have also been evaluated. The ΔH_{ads} and ΔS_{ads} values are thus found to be +38240 (J/mol) and ΔS_{ads} 138.43 J/K, respectively, while the ΔG_{ads} values is -3012.14 J in 298 K and it has been found that the reaction was spontaneous and endothermic in nature. On the other hand, Kinetic parameters have been investigated with pseudo first and second order. The result of experimental data indicates that pseudo second order equation fit better than the other.

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1. Introduction

Dyes, usually having a synthetic origin, are generally characterized by complete aromatic molecular structures which afford physicochemical, thermal, and optical stability (Dogan et al. 2006). The discharge of wastewaters containing dyes into river and streams is easily noticed since dyes are highly visible (Mohammed et al. 2014). Not only do they damage the aesthetic nature of the environment, but also they are commonly toxic to aquatic life (Akar et al. 2006). Various treatment processes including physical separation, chemical oxidation, and biological degradation have been widely investigated to remove dyes from wastewaters. Although there are many methods for the removal of the dyes, it is difficult to treat the wastewater through using traditional methods because most of the synthetic dyes are stable to photo-degradation, bio-degradation and oxidizing agents, etc. (Mahanta et al. 2008). The most commonly used methods for color removal are biological and chemical precipitation. Although biological procedures are widely utilized in the removal of color, they are very inefficient (Preethi et al. 2006) because of the low biodegradability of dyes (Vadivelan and Vasanth Kumar. 2005). Many techniques such as ion exchange (Raghu and Basha. 2007), chemical precipitation (Zhu et al. 2007), coagulation (Raghu and Basha. 2007), ozonation (Yan et al. 2009) and adsorption (Ansari et al. 2012) have been developed to remove these dyes from aqueous solution. Among these techniques, adsorption is considered as a preferred and effective technique due to the fact that it can deal with various concentrations of dyes and does not induce the formation of hazardous materials. The most widely employed adsorbent is activated carbon (Mohammad-khah and Ansari. 2009) due to its pore structure, high efficiency, and adsorption capacity for some dyes, but the cost and difficulty in separation after adsorption hinders its large-scale application (Uddin et al. 2009a).

In recent year, there has been considerable growth of interest in using environmentally friend adsorbent to enhance removal of dye from wastewater one of which is clay. Montmorillonite (MMT) is the most often

studied swelling clay mineral. The MMT layers have permanent negative charges because of the isomorphous substitution of, for instance, Mg²⁺ for Al³⁺ or, rarely, Al³⁺ for Si⁴⁺.

These net negative charges are balanced by exchangeable cations such as sodium and potassium between the clay layers in the gallery spaces (Shirini et al. 2012a).

In this study, functionalized surface of clay with Sulfonic acid (SANM) has been used as a newly reported derivative of Na⁺-Montmorillonite in which the number of negative charges is increased in enhancing the adsorption efficiency of methylene blue (MB). The aim of this work is to improve sorption characteristics of montmorillonite via modification using sulfonic acid. Montmorillonite was found a proper choice because it is available as clay. It was also found that a suitable substrate for the sorption of sulfonic acid in surface and negative charges are more and more in clays surface and convert this to best choice for dye removal because of efficiency and short contact time.

2. Materials and methods

2.1. Materials and reagents

Chemicals were purchased from Southern Clay Products, Fluka, Merck, and Aldrich chemical companies. A Metrohm pH meter (Model 827), with a combined double junction glass electrode, was used for pH measurements. The pH adjustments were carried out using diluted NaOH and HCl solutions. Methylene blue dye, termed as MB (chemical formula= C₁₆H₁₈N₃SCl, MW= 319.85 g/mol), was employed as a typical cationic dye for the current investigation. An UV-Vis spectrophotometer (Perkin-Elmer 35) was employed for the determination of residual MB concentration.

2.2. Preparation of SANM

A 500 mL suction flask, charged with 2.5 g Na⁺-montmorillonite (Southern Clay Products) and 10 mL CHCl₃, was equipped with a

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constant pressure dropping funnel containing chlorosulfonic acid (0.50 g, 9 mmol) and a gas inlet tube for passing HCl gas through an adsorbing solution i.e. water. Chlorosulfonic acid was added drop wise over a period of 30 min while the reaction mixture was stirred slowly in an ice bath. After addition was completed, the mixture was stirred for additional 30 min to remove all HCl. Then, the mixture was filtered and the solid residue was washed with methanol (20 mL) and dried at room temperature to obtain SANM as a white powder (Shirini et al. 2012a).

2.3. Characterization of SANM

SANM was prepared and characterized as the reported method in the literature (Shirini et al. 2012a; Shirini et al. 2012b).

2.4. Adsorption study

Batch adsorption experiments were carried out using a shaker. The effects of contact time, dye concentration and temperature on adsorption were investigated. For each experimental run, 0.3 g adsorbent and 50 mL of MB solution of known concentration were transferred into a flask, and agitated by shaker at a constant speed of 140 rpm with a required adsorption time. At predetermined time intervals, the solutions were centrifuged at 50 rpm for 10 min. The adsorption kinetics was determined by analyzing adsorption capacity from the aqueous solution at different time intervals. For adsorption isotherms, MB solution of different concentrations in the range of 200-1800 mg/L was agitated till the equilibrium was achieved. The effect of temperature on the adsorption characteristics was investigated by determining the adsorption isotherms at 303 to 353 K. Concentrations of dyes were determined by finding out the absorbance characteristic wavelength using UV-spectrophotometer. A standard solution of the dye was taken and the absorbance was determined at different wavelengths to obtain a plot of absorbance versus wavelength. The wavelength corresponding to maximum absorbance (λ_{max}) was determined from this plot. The λ_{max} for MB were found to be 640 nm. Calibration curves were plotted between absorbance and concentration of the dye solution. The adsorbed amounts (q) of MB were calculated by the following equation:

$$q = \frac{(C_0 - C_e)}{m} \quad (1)$$

where, C_0 and C_e are the initial and equilibrium concentrations of dye (mg/L), m is the mass of sorbent (g), and V is the volume of solution (L).

3. Results and discussion

3.1. Effect of initial MB concentration

The initial concentration of adsorbate in solution provides an important driving force in overcoming mass transfer resistance between the aqueous and the solid phases (Dogan et al. 2006).

Equilibrium adsorption studies have been performed to determine the capacity of the adsorbent; and the equilibrium is established when the concentration of adsorbate in the bulk solution is in dynamic balance with that on the surface (Bouberka et al. 2006). The effect of initial MB concentration on the adsorption onto SANM and the percentage dye removal are shown in Fig. 1. Hence, it appears that more MB was retained by the adsorbent and the adsorption mechanism also became more efficient, as the initial dye concentration increased, the percentage removal was higher at low concentration (Gupta et al. 2006). Moreover, the percentage of MB removal by the SANM sample at equilibrium indicates that the initial dye concentration has an important influence on the adsorption capacity of the SANM (Fig. 1). For example, at higher solution concentrations, 1600 and 1800 mg/L, the MB uptake shows a slight decrease. This result was obtained by 0.3 g of adsorbent in 10 min contact time.

3.2. Effect of contact time

The contact time being necessary to reach equilibrium depends on the initial dye concentration. It has been shown that the adsorption capacity increases with this concentration and the rate of adsorption on the surface should be proportional to a driving force times an area

(Almeida et al. 2009). The adsorption uptake versus contact time was investigated to find out the equilibrium time for maximum adsorption, as illustrated in Fig. 2. It is clear that the adsorption capacity increased promptly in the first time slot (0-10 min), but, after the contact time reached to 10 min, the adsorption capacity remained almost unchanged. Thereby, the equilibrium time of the studied experimental system was 10 min. Thus, a contact time of less than 10 min was invariably sufficient to reach to the equilibrium. The fast uptake of the dye molecules is due to solute transfer, as there are only adsorbate and sorbent interactions with negligible interference from solute-solute interactions. The initial rate of adsorption was therefore greater for high initial MB concentrations, the resistance to the dye uptake diminishing as the mass transfer driving force increased (Dogan et al. 2006).

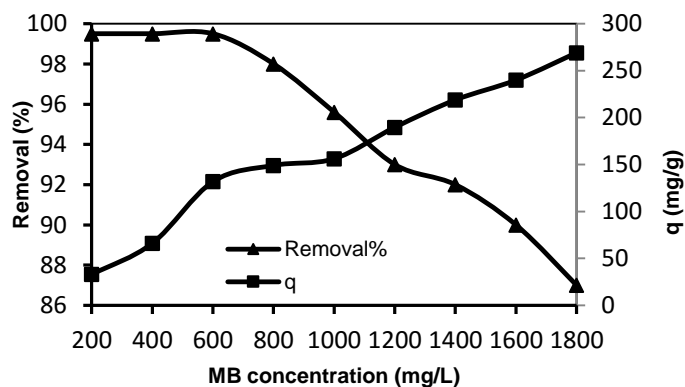


Fig. 1. Effect of initial MB concentration on the adsorption onto SANM ($T=298$ K, adsorbent = 0.3 g, $V = 0.05$ L).

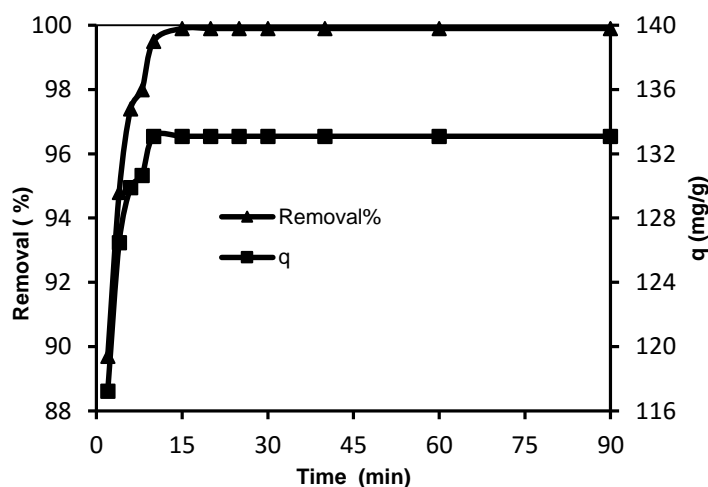


Fig. 2. Effect of contact time on the adsorption of MB onto SANM ($T=298$ K, $C_0=800$ mg/L, adsorbent = 0.3 g, $V = 0.05$ L).

3.3. Effect of adsorbent dosage

The effect of SANM concentration on MB adsorption at a contact time of 10 min was studied by varying the adsorbent dose from 0.1 to 0.75 g in 800 mg/L MB solution. The results are shown in Fig. 3. Increasing the adsorbent dosage enhances the percentage of removal of MB. Increased adsorbent concentration implies a greater surface area of SANM and, consequently, a greater number of possible binding sites. At adsorbent doses greater than 0.3 g, there was few changes in either the rate of attaining adsorption equilibrium of MB or the percentage removal of MB.

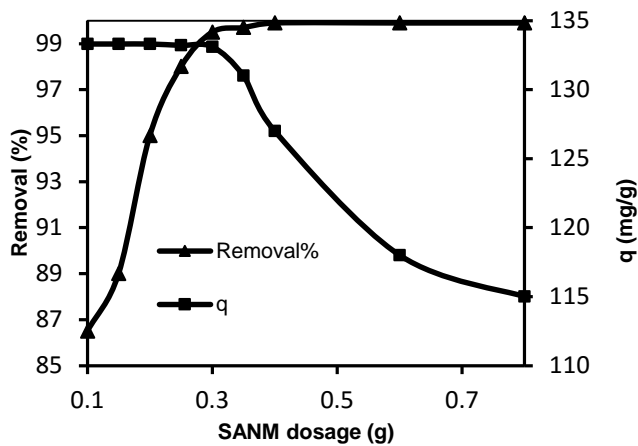


Fig. 3. Effect of SANM dosage on MB adsorption at a contact time of 10 min (T=298 K, C₀=800 mg/L, V= 0.05 L).

3.4. Effect of pH

Many studies suggest that pH is an important factor in the adsorption process (Seki and Yurdakoc. 2006). Some experiments were performed at 25 °C with 200 mg/L solutions to study the MB adsorption on SANM as a function of solution pH. The pH change by the addition of appropriate amounts of 0.1 M NaOH and HCl solutions. As it can be seen, this process is pH independent and initial pH=5 of MB is appropriate.

3.5. Adsorption isotherms

The adsorption isotherm suggests how an adsorbate distributes between the liquid phase and the solid phase when the adsorption process reaches to an equilibrium state and analysis of the equilibrium data is essential to optimize the adsorption system. Certain constants of an adsorption isotherm express the surface properties and affinity of the adsorbent. The adsorption equilibrium data was analyzed by Langmuir and Freundlich isotherms to evaluate the adsorption capacities of adsorbent. The Langmuir isotherm assumes that molecules adsorbed on an adsorbent do not react with each other and it is valid for monolayer adsorption on the surface of the adsorbent including a finite number of identical sites. A basic assumption is that sorption takes place at specific homogeneous sites within the adsorbent (Langmuir. 1918; Liu et al. 2013). A well-known linear form of Langmuir equation can be expressed as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_m C_e} \tag{2}$$

where, q_m represents the amount of adsorbate required to form a monolayer (mg/g) and q_e is adsorbate uptake at equilibrium (mg/g). C_e is the equilibrium concentration (mg/L), and b is Langmuir constant (L/mg). The values of b and q_m can be calculated from the intercept and the slope of the plot 1/q_e versus 1/C_e. An important feature of the Langmuir isotherm is R_L which is a dimensionless equilibrium parameter, also known as the separation factor, defined as (Hall et al. 1966).

$$R_L = \frac{1}{1+bC_0} \tag{3}$$

where, C₀ is the initial concentration of MB (mg/g). The value of R_L in the range of 0-1 indicates favorable adsorption, while R_L>1 represents unfavorable adsorption; R_L=1 hints linear adsorption while the adsorption process is irreversible in the event of R_L=0. The results given in Table 1 show that the adsorption of methylene blue onto SANM is favorable.

As also seen in Table 1, the adsorption capacities of SANM for methylene blue is 500 mg/g. Previously, some researchers investigated several adsorbents such as montmorillonite clay (Almeida et al. 2009), Luffacylindrica fibers (Demir et al. 2008), tea waste (uddin et al. 2009b), MMT/CoFe₂O₄ composite (Lunhong et al. 2011), Sewage Sludge Based Granular Activated Carbon (Liu et al. 2013) and activated carbon (Legrouiri et al. 2005) for the removal of methylene blue from aqueous solutions. By comparing the results obtained in this study with those in the previously reported works, Table 2 on adsorption capacities of various low-cost adsorbent and activated carbon in aqueous solution for methylene blue, it can be stated that the findings of the current study are really good.

The Freundlich isotherm is valid for multilayer adsorption on the surface of an adsorbent, indicating non-ideal adsorption on heterogeneous surfaces. The linear form of the Freundlich equation is given as follows (Hall et al. 1966).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

where, K_F and 1/n are Freundlich constants correlated to adsorption capacity and adsorption intensity of an adsorbent, respectively. The intercept and slope of the plot of log q_e against log C_e can be obtained K_F and 1/n. Correlation coefficients (R²) and other parameters computed by fitting the experimental equilibrium data to Langmuir and Freundlich isotherm equations were tabulated in Table 1. The best-fit model was determined corresponding to R² value. From Table 1, checking the R² values indicated that Langmuir model was more suitable for the experimental data due to higher R² values, nearly close to unit at this temperature, suggesting the monolayer coverage of MB on the surfaces of adsorbent (Langmuir. 1918). Furthermore, the experimental adsorption capacities (q_e) were close to theory maximum adsorption capacities (q_m), and the time-rate curves substantially validated the conclusion mentioned above. The values of R_L were in the range of 0-1, indicating that the adsorption process was favorable.

Table 1. Isotherm constants for MB on adsorbents.

q _m (mg/g)	Langmuir model			Freundlich model		
	b(L/mg)	R ²	R _L	k _f (mg/g)(L/mg) ^{1/n}	N	R ²
500	0.01	0.984	0.11	28.5	2.35	0.946

3.6. Thermodynamic studies

The thermodynamic parameters are important for a better understanding of the effect of temperature on adsorption (Seki and Yurdakoc, 2006). Hence, K_C can be used to estimate the enthalpy change accompanying adsorption, ΔH_{ads}, i.e., the standard enthalpy change of adsorption at a fixed surface coverage (Rytwo et al. 2006). The thermodynamic parameters ΔH_{ads}, ΔS_{ads}, and ΔG_{ads} associated with the adsorption process can be determined using the following equations. The standard Gibbs' free energy change of adsorption, ΔG_{ads} can be related to the equilibrium, K_C, by:

$$\Delta G_{ads} = -RT \ln K_C \tag{5}$$

where, R is the gas constant (R = 8.314 J/mol K). A convenient form of the van't Hoff equation (Seki and Yurdakoc. 2006) then relates K_C to the standard enthalpy and entropy changes of adsorption, respectively.

$$\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{6}$$

On the basis of a plot of ln K_C versus 1/T (Eq. 6), ΔH_{ads} can be estimated from the slope and ΔS_{ads} from the intercept of what should be a straight line passing through the points. Fig. 4 shows just such a plot

with a correlation coefficient of 0.987. The ΔH_{ads} and ΔS_{ads} values are thus found to be +38240 (J/mol) and ΔS_{ads} 138.43 J/K, respectively, while the ΔG_{ads} value is -3012.14 J in 298 K. The positive value of ΔH_{ads} confirms the endothermic nature of the adsorption process, as has been found in most cases.

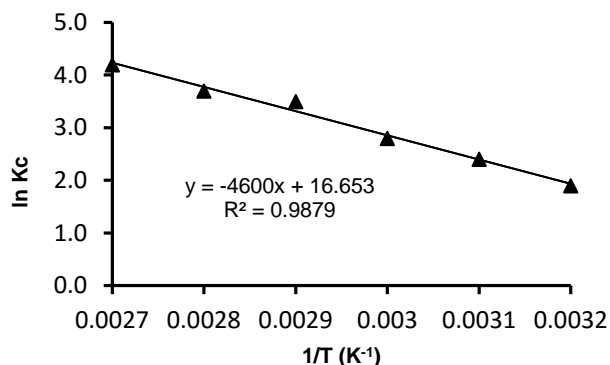


Fig. 4. Plot of $\ln K_c$ versus $1/T$ of adsorption of MB onto SANM ($T=298$ K, $C_0=800$ mg/L, adsorbent = 0.3 g, $V = 0.05$ L, contact time=10 min).

This feature may be an indication of the occurrence of monolayer adsorption (Rytwo et al. 2006). The positive value of ΔS_{ads} corresponds to an increased degree of freedom in the system as a result of adsorption of the MB molecules. There are various possible explanations. Another issue is that structural changes take place as a result of interactions of MB molecules with active groups in the SANM surface. Elsewhere comes the suggestion of increased randomness at the solid-solution interface reflecting principally the extra translational entropy gained by the solvent molecules previously adsorbed on the clay but displaced by the adsorbate species (Tahir et al. 2006).

3.7. Adsorption kinetics

In order to investigate the mechanism of sorption and potential rate controlling steps such as mass transport and chemical reaction processes, kinetic models have been used to test experimental data. These kinetic models included the pseudo-first order equation, the pseudo-second order equation. The pseudo-first order equation expressed as follows:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (7)$$

The parameter k_1 (1/min) is the rate constant of the pseudo-first-order model. Due to equation (7) the experimental data, the equilibrium sorption capacity, q_e , must be known. In many cases, q_e is unknown and, as chemisorptions tend to become immeasurably slow, the amount sorbed is still significantly smaller than the equilibrium amount. If the rate of sorption is a second order mechanism, the pseudo-second order chemisorptions kinetic rate equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (8)$$

k_2 (g /mg min) is the rate constant of the pseudo-second-order models, q_e and k_2 can be obtained from the plot t/q_t versus t .

From the pseudo-second-order rate constants, k_2 , at a different temperature and using the Arrhenius equation (Eq. 9), it is possible to gain some insight into the type of adsorption.

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (9)$$

Here E_a is the activation energy (J/mol), k_2 the pseudo second-order rate constant for adsorption (g/mol s), A the temperature-independent Arrhenius factor (g/mol s), R the gas constant (8.314 J/Kmol), and T the solution temperature (K). The slope of the plot of $\ln k_2$ vs. $1/T$ can then be used to evaluate E_a . Low activation energies (5-40 kJ/mol) are characteristic of physical adsorption, while higher ones (40-800 kJ/mol) suggest chemisorptions (Almeida et al. 2009). The present results give $E_a = +53.98$ kJ/mol for the adsorption of MB onto SANM (Fig. 5), indicating that the adsorption is chemisorptions.

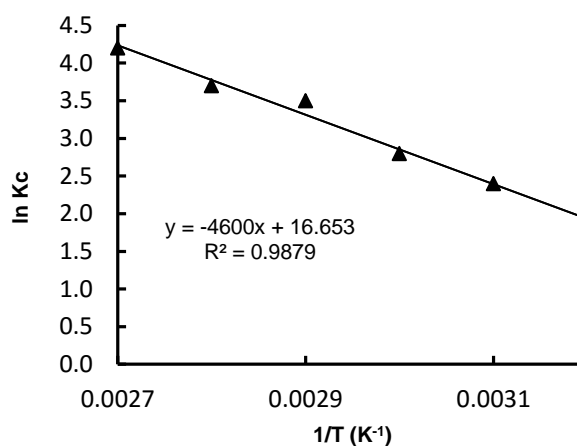


Fig. 5. Plot of $\ln K_c$ versus $1/T$ of adsorption of MB onto SANM ($T=298$ K, $C_0=800$ mg/L, adsorbent = 0.3 g, $V = 0.05$ L, contact time=10 min).

Based on the parameters in Table 3, the R^2 values of pseudo-second-order model were found to be higher than the other models, which indicated that the experimental data was fitted to pseudo-second-order kinetic model for MB onto SANM. In addition, the calculated q_e values from pseudo-second-order model were close to those of experimental q_{exp} , validating the results mentioned above.

Table 2. Previously reported adsorption capacities of various adsorbents for methylene blue.

Adsorbent	Adsorption capacity (mg/g)	Initial concentration of MB (mg/L)	Contact time (min)	references
SANM	500	800	10	This work
Activated carbon	435	200	1200	(Legrouiri et al. 2005)
Luffacylindrica fibers	156.6	47-52	1500	(Demir et al. 2008)
Montmorillonite clay	86.32-348.87	200-1000	30	(Almeida et al. 2009)
Tea waste	85.16	20-50	300	(Uddin et al. 2009b)
MMT/CoFe ₂ O ₄ composite	97.75	100	40	(Lunhong et al. 2011)
SSGAC*	131.8	400	1440	(Liu et al. 2013)

* Sewage Sludge Based Granular Activated Carbon

Table 3. Kinetic parameters for the removal of MB onto SANM.

Pseudo-first order			Pseudo-second order		
R ²	K ₁ (1/min)	q _{exp} (mg/g)	R ²	K ₂ (g/mg.min)	q _{exp} (mg/g)
0.973	0.32	129.91	0.999	0.025	142.85

4. Conclusion

In this article, the authors have reported a new, efficient, and environmentally friendly adsorbent (SANM) in water treatment which is independent to pH and reaches to equilibrium in a contact time of less than 10 min, low cost of the sorbent, and simple procedure. This process obeyed pseudo-second-order kinetics with an activation energy of +53.98 kJ/mol, consistent with the description of the process as involving chemisorptions.

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