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Separation of chromium from water samples using eggshell powder as a low-cost sorbent: kinetic and thermodynamic studies

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ABSTRACT

Chromium is one of the hazardous pollutants in industrial effluents. The aim of this research is to investigate feasibility of using waste eggshells for the removal of Cr(VI) ions from its aqueous solutions. Characterization of crushed and sieved eggshell have been carried out using scanning electron microscope, Fourier transform infrared spectroscopy, X-ray diffraction, X-ray fluorescence, etc. analysis. The effect of pH, Cr(VI) ions concentration, amount of eggshell, contact time, temperature, etc. parameters have been investigated on the adsorption and it has been found that the maximum removal (about 93%) of Cr(VI) onto eggshells can be achieved at 25°C and pH 5 in 90 min. Freundlich and Langmuir adsorption isotherm models e have been verified using experimental data. Results also include calculation of thermodynamic parameters like, change in enthalpy (ΔH^0), change in entropy (ΔS^0), and change in free energy (ΔG^0) of the ongoing adsorption process. Chromium sorption kinetics is also found to be fitted in pseudo-first-order kinetic model. Results clearly indicate that the waste material eggshell, a solid waste from the food industry, can be very effectively used as a sorbent for the removal of chromium ions from its aqueous solutions.

Keywords: Adsorption; Eggshell; Chromium; Isotherm; Kinetics

1. Introduction

Due to good solubility in water and its behavior as oxidizing agent, hexavalent chromium i.e. Cr(VI) poses acute toxicity towards humans and animals [1]. It is a well-established fact that once Cr(VI) reaches to blood stream, it damages kidney, liver, and blood cells of humans through oxidation reactions and patient leads to hemolysis, renal, and liver failure [2,3]. Cr(VI) is leads to allergic reactions in the human beings [4,5], and even at low concentration it can cause diseases such as encephalopathy, anemia, hepatitis, and nephritic syndrome [2,3]. Cr(VI) also possesses carcinogenicity and can damage DNA of humans and animals [4].

Cr(VI) has wide range of applications in industrial field. It is used in electroplating, cement, steel, paint, dyes, aluminum, leather tanning, metal finishing, and chromate manufacturing industries [6]. Thus, the effluents from these industries, when mix with the soil or surface water; create health hazards to the mankind. It is therefore needed to develop methods for environmental cleanup and remediation, so that Cr(VI) is safely removed from the water. In past few years, many techniques such as chemical precipitation,

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ion-exchange, membrane filtration, coagulation–flocculation, flotation, electrochemical, ultrafilteration, etc. have been used by various workers [7–10]. However, most of these methods are neither cost effective nor safe and easy to handle. The research of last two decades has clearly established that adsorption is the most convenient and economic method for the toxic metal removal from the wastewater [11–13]. This period has also witnessed sincere efforts from global researchers to search low-cost adsorbents and large numbers of waste materials have been improved waste materials into potential adsorbents [14,15].

Eggshell is a waste material emerging in large quantity from food industries. In recent past, this material has proved its significance as natural sorbent to remove pollutants wastewater but most of these attempts are either for the removal of colored dyes or phenol and its derivatives [16–18]. Keeping these in view, it is therefore considered worthwhile to carry out a systematic study to remove hazardous metal ion Cr(VI) from its aqueous solutions using eggshell as adsorbent.

2. Material and methods

2.1. Preparation of adsorbent material

The waste eggshells were collected from local bakery workshop. The procured eggshells were first thoroughly washed by tap water and then rinsed several times in distilled water. Washed eggshells were then dried by keeping in an oven at room temperature for overnight. From the dried eggshells, membranes were carefully removed and discarded. Eggshell material thus obtained was washed with de-ionized water and then dried at 70˚C for about 12 h. Finally, this material was mechanically granulated by a crusher, sieved and with and stored in desiccator until experiments.

2.2. Chemicals and Batch experimental

The stock solution of 1 g/L concentration of Cr(VI) was prepared by dissolving $K_2Cr_2O_7$ in the deionized water. During adsorption experimentation, Cr(VI) solutions of different concentrations were taken into series of 250 ml stopper conical flask and dried eggshell of known quantity was added into each. The pH and temperature of each solution mixture were kept constant and the mixture was then thoroughly mixed on a mechanical shaker for a predetermined period of time. When the shaker is stopped, the uptake of Cr(VI) was determined using the spectrophotometer DR-5000. All the experiments were conducted in triplicate, and the average results are reported in this paper.

3. Results and discussion

3.1. Characterization of sorbent

The scanning electron microscope (SEM) photographs (Fig. 1) exhibit a clear view of structural morphology of the eggshell and it can be easily observed that eggshell structure is partly porous and almost homogeneous in shape. The X-ray fluorescence analysis clearly displays the presence of keratin fiber, Ca, Si, Na, S, and Mg as major constituents in the eggshell (Table 1).

In order to delineate those functional groups and absorption bands present in the eggshell structure, which are responsible for Cr(VI) adsorption, Fourier transform infrared spectroscopy (FTIR) spectrum of eggshell was monitored in the range of 500–4,000 cm^{-1} (Fig. 2). Fig. 2 indicates that IR bands corresponding to principal functional groups of the adsorbent are exhibited between 710 and 1,500 cm^{-1}. The peaks at 712.83 and 875.59 correspond to P–O and S=O stretching vibrations [19,20], while the band at 1425.09 cm^{-1} denotes C=O stretching vibration [21,22]. This further clarifies that calcite is the fundamental constituent of the eggshell [22]. The well-defined broad peak at

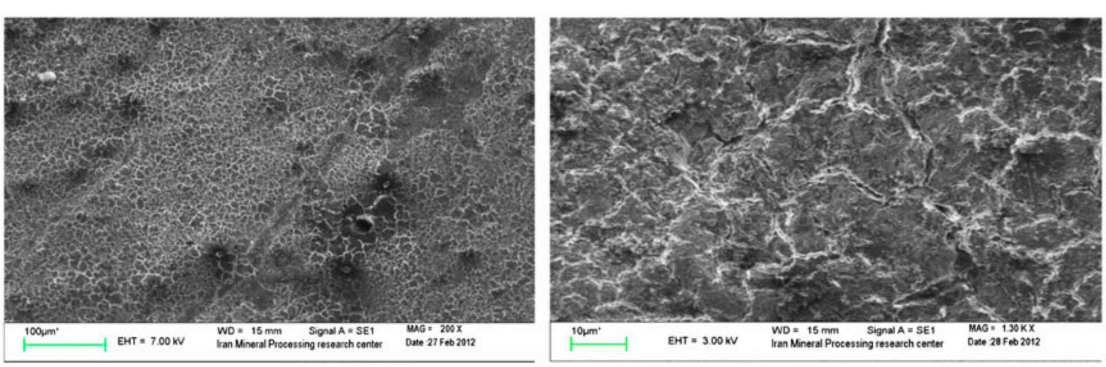

Fig. 1. SEM photographs of the sorbent-eggshell.

Table 1
Chemical constituents of eggshell

Element	$CaCO_3$	L.O.I	Si	Mg	Al	Na	S
(%)	54.32	15.87	0.45	0.64	0.08	0.14	0.43

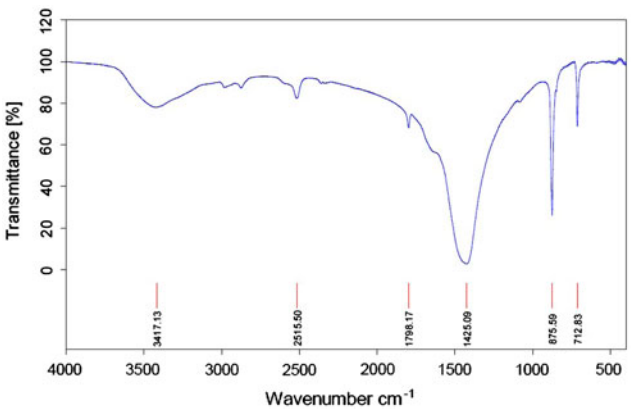

Fig. 2. FTIR spectrum of the sorbent-eggshell.

$3417.13\,cm^{-1}$ is elated to –OH group stretching vibrations, where broad range of frequencies are arising due to presence of free groups of hydroxyl and linked O–H bands of carboxylic acids.

The crystal structure of eggshell was analyzed by X-ray diffraction (XRD) and its diffraction pattern is shown in Fig. 3. The XRD pattern displays six characteristic peaks at $2\theta = 34.5^\circ$ (main peak), 42.2˚, 46˚, 50.9˚, 56˚, and 57.8˚ and corroborates the presence of calcite ($CaCO_3$) in the structure of eggshell.

3.2. Effect of pH and dosage of sorbent

Fig. 4 displays effect of sorbent dosage and pH of the solution on the adsorption of Cr(VI) by eggshell. It is found that with the increase in sorbent amount the sorption of Cr ions increases due to increase in active and vacuous areas on the surface of the eggshell [23].

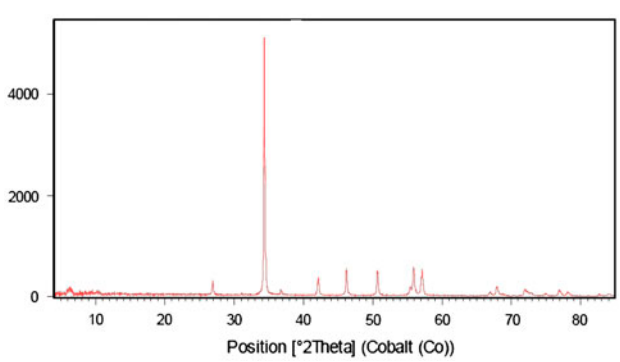

Fig. 3. X-ray diffraction pattern of the sorbent-eggshell.

Fig. 4 also shows that with increase in pH from 3 to 5, Cr(VI) adsorption increases but beyond pH 5 it almost linearly decreases till pH 11.

It is pertinent to note that during the adsorption process of heavy metals, pH of the solution plays a very prominent role as it can affect the ionization of the metal ion and vary the surface charge of the sorbent. Thus, in the present case variation in pH will affect the number of binding sites on the membrane surface and the chemical property of Cr(VI) ions in the solution. Thus, low Cr(VI) removal at higher pH may be attributed to reduction in protonation, which enhances electrostatic repulsive force between Ca^{+2} at eggshell and Cr(VI), thereby retards diffusion and adsorption [24,25].

3.3. Effect of contact time and initial concentration

The adsorption of Cr(VI) onto eggshell was also investigated at different contact times at pH 5. It is found that the percentage removal of Cr(VI) increases rapidly with time up to 90 min and thereafter becomes constant (Fig. 5). The rapid and high sorption rate during initial period is mainly due to the availability of active sites on the sorbent which facilitates accumulation of Cr(VI) ions on the eggshell [25,26]. Fig. 5 also exhibits that with the rise in Cr(VI) concentration adsorption decreases. The maximum sorption in low concentration may be credited to the availability of more active bands on the sorbent surface and increase in the mass transfer velocity [27].

3.4. Adsorption isotherms

In order to understand the adsorption behavior of Cr(VI) onto eggshells, Freundlich and Langmuir adsorption isotherm models were analyzed through

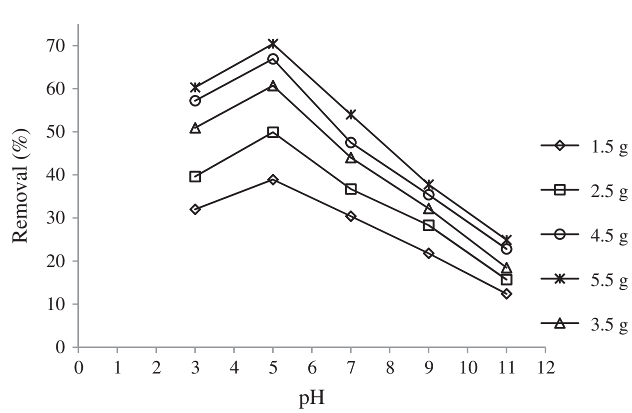

Fig. 4. Effect of pH and sorbent dosage on the removal of Cr(VI) by eggshell (concentration = 15 mg/L, contact time = 120 min, and temperature = 25℃).

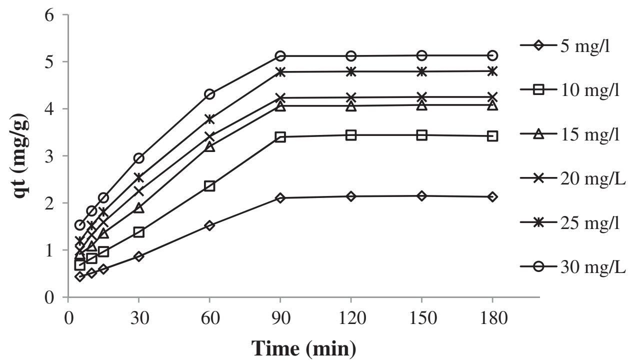

Fig. 5. Effect of contact time and initial concentration of Cr(VI) on the removal of Cr(VI) by eggshell (pH = 5, sorbent dosage = 3.5 g, and temperature = 25 °C).

the experimental data. Following linear forms of Freundlich (Eq. (1)) and Langmuir (Eq. (2)) adsorption isotherms [25] are used:

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

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_oC_e} \tag{2}$$

where q_e is the amount of adsorbate in soil phase (mg/g), C_e is the equilibrium concentration of adsorbate in liquid phase (mg/L), K_F ($\mathrm{mg}^{1-1/n}\mathrm{L}^{1/n}$/g), and $1/n$ are the Freundlich constants. q_m is the maximum adsorption capacity (mg/g) and b (L/mg) is the Langmuir constant.

A graph between log C_e vs. log q_e (Fig. 6(a)) gives straight line verifying thereby the ongoing adsorption to follow Freundlich model. Similarly, verification of Langmuir adsorption model is concluded by obtaining a straight line in the C_e vs. C_e/q_e plot (Fig. 6(b)). The intercept and slope of both the straight lines gave respective values of Freundlich and Langmuir constants, which are presented in Table 2. Value of Langmuir constant is helpful in calculating various thermodynamic parameters, while high value of K_f indicates good affinity of the Cr(VI) ions with eggshell and obtained value of the constant (n) indicates an idealistic adsorption.

On comparing the Freundlich and Langmuir isothermals, it can be expounded that Freundlich adsorption isotherm is more desirable as compared to the Langmuir, which is also evident from the R^2 values presented along with the graphical trend.

3.5. Thermodynamic study

Thermodynamic parameters like change in free energy (ΔG^0), change in enthalpy (ΔH^0), and change

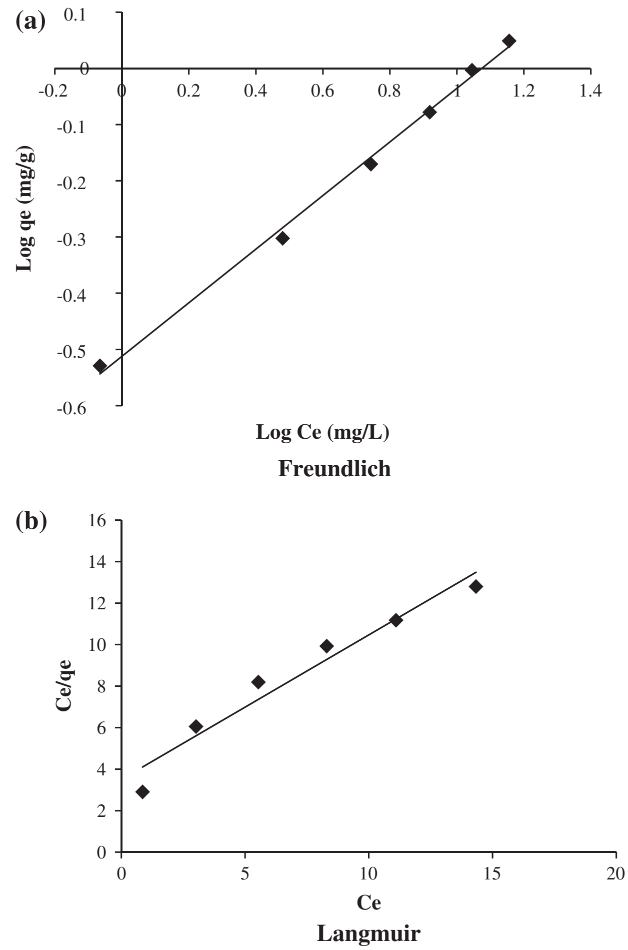

Fig. 6. Freundlich and Langmuir adsorption isotherm for the Cr(VI) removal.

Table 2
Calculated values of Freundlich and Langmuir constants for Cr(VI) adsorption over eggshell

Freundlich constants			Langmuir constants		
K_f (mg/g)	n (mg/L)	R^2	q_m (mg/g)	b (mg/L)	R^2
3.256	2.097	0.995	1.45	0.20	0.950

in entropy (ΔS^0) were calculated by using following equations:

$$\Delta G^0 = -\mathrm{RT} \ln K_d \tag{3}$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{\mathrm{RT}} \tag{4}$$

where equilibrium constant k_d was calculated by q_e/C_e at temperatures 20–60 °C [28], R is the universal gas constant (8.314 J/mol K), and T is the temperature (K). Parameters change in enthalpy (ΔH^0) and change in

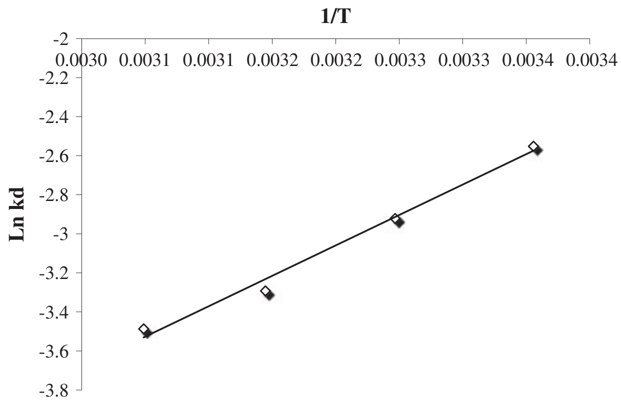

Fig. 7. Temperature (K) vs. ln K_d plot for the adsorption of Cr(VI) onto eggshell.

entropy (ΔS^0) are calculated from the slope and the intercept of the linear plot of ln k_d vs. $1/T$ (Fig. 7) and their values are presented in Table 3 along with values of change in free energy (ΔG^0).

The negative value of ΔH^0 confirms the exothermic nature of the studied system, while the negative values of ΔG^0 indicate the feasibility and spontaneity of the ongoing adsorption process. The positive value of ΔS^0 indicates increased randomness at the solid solution interface.

3.6. Adsorption kinetics

In order to design a valid adsorption process, it is highly necessary to augury the kinetics of the continuous adsorption process. There are several kinetic models such as pseudo-first-order, pseudo-second-order, etc. [29]. For determining the kinetics of adsorption either infinite bath system or finite bath method are usually employed. It is now well established that out of the two techniques, batch technique is more effective and accurate and considered suitable to carry out kinetic experiments because of ease of operation, adaptability to small volume work, and time effectiveness. Keeping the same in view, in the present paper pseudo-first-order and pseudo-second-order kinetic models has been verified by carrying out experiments under batch technique (Tables 4 and 5).

3.6.1. Pseudo-first-order model

The sorption of ions from a liquid phase to a solid phase can be perceived as a reversible reaction with equilibrium being established between the liquid phase and the sorbent. A simple kinetic evaluation of such an adsorption is pseudo-first-order equation [30]. In this kinetics, it is proposed that initially there is no sorbate ions present on the surface of the sorbent and as time progresses the sorbate ions are accumulating over the surface of sorbent. The equation given below represents pseudo-first-order rate expression [31],

Table 3
Calculated values of various thermodynamic parameters for Cr(VI) adsorption over eggshell

$1/T$	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)
		−374.6	−1.56
298	−6,320		
308	−7,479		
318	−8,703		
328	−9,507		

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \times t \tag{5}$$

In the above equation, q_e and q_t denote the amount adsorbed at equilibrium and at any time t, respectively, and k_1 is the first order rate constant. The graph was plotted between log ($q_e - q_t$) and time, the slope of which gives the value of k_1 (Fig. 8). It was observed that with increase in concentration of the Cr (VI) values of first-order rate constant remains almost constant (Table 4).

3.7. Pseudo-second-order model

A pseudo-second-order kinetic model is based on adsorption equilibrium capacity of the adsorption system. It was used on the experimental data for better exposition of the continuous kinetics. The model indicates that the sorption capacity of the sorbent is proportional to the number of active sites occupied on its surface

Pseudo-second-order kinetic is described as follows (Eq. (3)) [29,30]:

$$t/q_t = 1/k_2 q_e^2 + 1/q_e t \tag{6}$$

The value of k_2 and q_e can be described from the slope and the intercept of the plot t/q_t vs. t, respectively.

On comparing the R^2 values obtained for first-order and second-order kinetics (Table 5) it can be easily concluded that the ongoing adsorption proceeds follows pseudo-first-order rate kinetics. It is also interesting to note experimental values of q_e were close to calculated values of q_e.

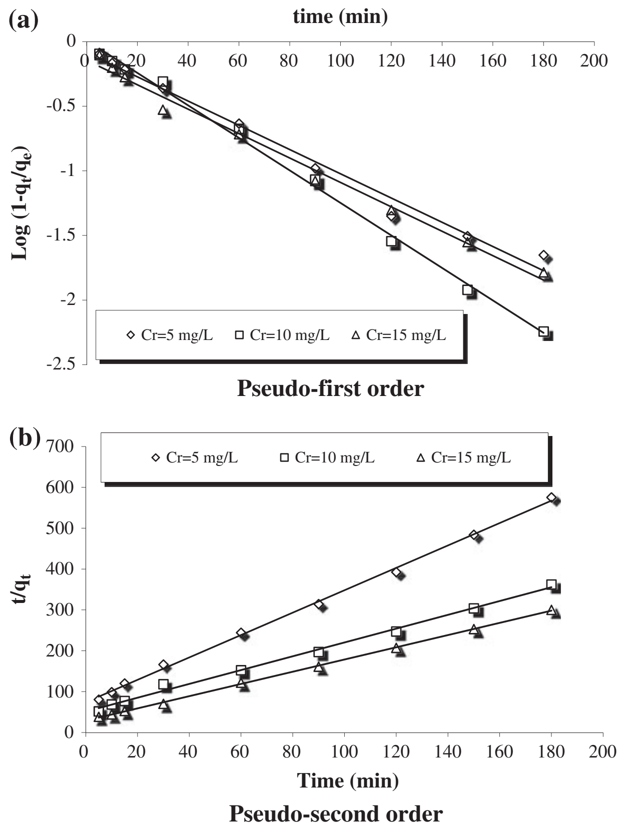

Fig. 8. Plots for kinetic models for the adsorption of Cr(VI) onto eggshell.

Table 4
Values of pseudo-first-order rate constants at different concentrations of Cr(VI)

Initial Cr(VI) concentration (mg/L)	k_1 (min^{-1})	q_e (mg/g)	R^2
5	0.004	0.32	0.99
10	0.004	0.50	0.99
15	0.004	0.60	0.99

Table 5
Values of pseudo-second-order rate constants at different concentrations of Cr(VI)

Initial Cr(VI) concentration (mg/L)	K_2 (min^{-1})	q_e (mg/g)	R^2
5	0.1	0.32	0.98
10	0.05	0.48	0.965
15	0.08	0.60	0.95

4. Conclusion

The results presented in the paper clearly indicate that waste material eggshell can be used as potential adsorbent for the effective and fast removal of the hazardous Cr(VI) ions from water and wastewater. The sorption depends upon pH of the solution, concentration of Cr(VI), amount of eggshells, temperature, contact time, etc. Optimum removal of Cr(VI) at any temperature can be achieved, when 3.5 g eggshells are added into 30 mg/L concentration solution of Cr(VI) at pH 5.0 and this mixture is thoroughly shaked for 90 min. Results also indicate that the ongoing adsorption follows Freundlich as well as Langmuir adsorption isotherms. The change in enthalpy and change in entropy of the Cr(VI)—eggshell adsorption system are found as −374.6 (kJ/mol) and −1.56 (kJ/mol), respectively. The kinetic measurements reveal that adsorption follows pseudo-first-order rate reaction and rate constant of the process is 0.004 min^{-1}.

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