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Adsorption of Zn(II) on activated red mud: Neutralized by CO₂

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Abstract

In this study, caustic red mud was neutralized using CO₂ sequestration. Batch adsorption study was conducted to investigate the ability of activated CO₂-neutralized red mud (ANRM) for the adsorption of Zn(II) ions from the aqueous solutions. The experiments were carried out with respect to adsorbent dose, pH, contact time, initial Zn(II) concentrations, kinetics, Langmuir and Freundlich isotherms. The characterization of CO₂ neutralized red mud and mechanisms of Zn(II) adsorption on ANRM were studied by using TG-DSC, SEM/EDX, BET, AAS and chemical methods. Adsorption kinetic studies revealed that the adsorption process followed pseudo-second-order kinetics. The adsorption data were fitted to linearly transformed Langmuir isotherm with R^2 (correlation coefficient) > 0.98.

Keywords: Red mud; CO₂; Zinc; Kinetics; Langmuir isotherm

1. Introduction

Zinc is released into aquatic and soil environments largely from various natural and anthropogenic activities. Metal mining, metallurgy industries, coating, alloy industries, and sludge produce large quantities of wastewater containing high concentration of Zn(II) ions. Zn(II) is toxic for animals and plants at high concentrations. Long-term exposure to Zn(II) can cause hazardous effects in animals, and plants [1-3]. Therefore, World Health Organization (WHO) has recommended the maximum permissible limit for Zn(II) in drinking water is 5 mg L^{-1} [4].

Previous research has revealed that the adsorption of Zn(II) ions is rising for demand of standard drinking water. Thus, there is growing interest for the development of low-cost materials and methods for removal of Zn(II) ions from drinking water or industrial effluents before it may cause significant contamination. Although many different methods such as precipitation, colloid flotation, ion-exchange, ultrafiltration, and reverse osmosis has been used for removal of heavy metal ions [5], whereas the process based on adsorption methods are promising, due to low cost and high removal efficiency. Different types of adsorbents have been used for removal of zinc such as: soil [6], clay [7,8], hydroxyapatite [9], red mud [10–12].

Red mud (RM) is a waste product formed after caustic digestion of bauxite during the extraction of alumina. The storage and maintenance of highly caustic red mud is a challenging environmental problem in the alumina industry [11,12]. But, its utilization for environmental benefit can also enhance the socio-ecological-economical value of alumina industries.

With our knowledge from literature survey, the adsorption of Zn(II) ions from aqueous solutions using activated CO_2 -neutralized red mud has not been reported. The objective of this study is to characterize the CO_2 -neutralized red and adsorption of Zn(II) on the ANRM. Also,

investigate the % removal of these ions from the aqueous solutions by batch experiments. The effect of various parameters such as adsorbent dose, time, pH, effect of initial concentration, kinetics, Langmuir and Freundlich isotherms, etc. were examined on the adsorption of Zn(II) ions from aqueous solutions by ANRM.

2. Materials and methods

2.1. Materials

All chemicals, including HCl, NaOH, HNO₃, KBr, zinc standard solution of 1000 mg/L used in the present study were of analytical grade and obtained from Merck (Germany), zinc chloride anhydrous (ZnCl₂) from Finar Chemical Ltd., cadmium chloride monohydrate (CdCl₂.H₂O, Rankem), lead nitrate purified (Pb(NO₃)₂, Merck), citric acid-hydrate crystal extra pure (C₆H₈O₇.H₂O, Merck). In all experiments, distilled water was used for preparation, dilution and analytical purposes of the solutions. Zn(II) stock solutions of 1000 mg L⁻¹ were prepared separately by dissolving appropriate amount of ZnCl₂ in 1 L of distilled water. Test solutions of Zn(II) having different concentrations (5-100 mg L⁻¹) were prepared from the stock solutions by proper dilution with distilled water.

2.2. Adsorbent preparation

The fresh red mud used in this study was obtained from R&D Laboratory of NALCO, Damanjodi, Orissa, India, in the form of dried-clay. The chemical compositions of the RM based on the dry weight are analyzed and found to contains Fe₂O₃ (54%), Al₂O₃ (13%), SiO₂ (7%), Na₂O (8%), TiO₂ (3.5%). The RM was neutralized using sequestration of CO₂ gas. The pH of RM suspension was decreased from 11.8 to 8.45. This partially neutralized red mud (NRM) sample was dried at 110 °C for 2 h and calcintaed at 500 °C for 2 h which is referred as activated neutralized red mud (ANRM).

2.3. Characterization of adsorbent

The surface micro-morphology of materials was investigated using a high resolution scanning electron microscope (SEM) and qualitative element composition was analyzed using energy dispersive X-ray (EDX) operated at an accelerating voltage of 20 keV, by JOEL model JSM-6480LV (Japan).

The BET surface area was measured at liquid N₂ temperature using the Brunauer–Emmett–Teller (BET) surface area analyzer (Quantachrome AUTOSORB–1, USA). All samples were degassed at 150 °C in vacuum. Helium was used as carrier gas and surface area was measured by N₂ adsorption–desorption method. Particle size of the red mud was measured using Master Sizer 33370-45 (Malvern, UK).

The thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) analysis were carried out using NETZSCH STA 409C, Germany. In this analysis, 30 mg of sample was used and alumina was used as reference. The sample was heated in an Al₂O₃ crucible at a heating rate of 10.0 °C min⁻¹ from 25 to 900 °C. The pH measurements of aqueous solutions were made using a calibrated Orion 2 Star Bench top pH meter. Quantitative analysis of the Zn(II) in the filtrate, after adsorption was determined by using atomic absorption spectrometer (AAS, PerkinElmer, AAnalyst 200, USA) using standard method. Calibration was achieved using dilutions prepared from a commercially available 1000 mg L⁻¹ standard zinc solutions [13,14].

2.4. Batch experiments

Batch experiments were carried out at room temperature (25 ± 2 °C) using 100 mL stoppered polylab plastic bottles. 0.2 g of ANRM adsorbent was weighted and put into the different plastic bottles, into which 50 mL of Zn(II) solutions with initial concentration 30 mg L⁻¹ were added separately. The bottles were capped tightly for all tests to avoid change in concentration, due to

evaporation. The pH was adjusted to the desired level by adding required amount of with 0.1 M NaOH or 0.1 M HCl solutions. A number of experimental parameters such as adsorbent dose (1-10 g L⁻¹), contact time (1–24 h), initial concentration of adsorbate 30 mg L⁻¹ and pH (3–9) which affecting the adsorption process have been studied to optimize the removal process. The solutions were stirred using magnetic stirrer at about 180 rpm for 24 h until the adsorption equilibrium time was reached.

The adsorption of Zn(II) ions from multimetal solutions containing Zn(II), Pb(II), Cd(II) and organic matter (citric acid) was carried out at optimum conditions such as pH 6, contact time 8 h, adsorbent dose 0.2 g/50 mL of multimetal solutions of concentration 30 mg L⁻¹. The multimetal solutions of concentration 30 mg L⁻¹ were prepared by adding equal amount (30 ml) from each of stock solutions (1000 mg L⁻¹) ZnCl₂, CdCl₂.H₂O, Pb(NO₃)₂, C₆H₈O₇.H₂O and by proper dilution with distilled water.

After stirring, the solutions were allowed to settle for 10 min and the samples were centrifuged at 3000 rpm for 20 min and filtered through Whatman 42 filter paper. The filtrate was used for the analysis of remaining Zn(II) ions concentration in the solution. The amount of Zn(II) adsorbed (removal) was calculated as follows:

$$\% \text{ adsorbed} = \frac{[C]_i - [C]_f}{[C]_i} \times 100 \quad (1)$$

where $[C]_i$ and $[C]_f$ are the initial and final concentrations of the Zn(II) in the aqueous solutions (mg L⁻¹), respectively.

3. Results and discussion

3.1. Characterization of adsorbent

Fig. 1 shows the particle size distribution of red mud particles. The horizontal axis denotes the diameter of the particles distributed over the range of 0.1–160 μm , with volume-based peaks at about 0.31 μm and 48.27 μm . The elements composition of the by-product in wt% C(1.10), Na(6.01), Al(8.52), Si(5.35), Ti(2.27), Fe(35.13), Zr(1.40), O(33.22). The BET-N₂ surface area of RM, NRM and ANRM were found to be 31.70, 59.33 and 68.22 $\text{m}^2 \text{g}^{-1}$, respectively. The surface areas of NRM and ANRM were increased, due to acidic CO₂ and removal of volatile materials by thermal treatment at 500 °C, respectively.

TG and DSC analyses of neutralized red mud were carried out and results are presented in Fig. 2. First weight loss from TG analysis was found to be 1.41%. This weight loss was probably due to the physically adsorbed water on the neutralized red mud. The endothermic process peak was at 283 °C and the corresponding weight loss from TG analysis was found to be 8.55%. This may be due to loss of loosely bound water, and strongly bound water. The third weight loss was 2.00% may be due to remaining evolution of H₂O and CO₂.

SEM micrograph (Fig. 3) provides the surface micro morphology of the ANRM. Some mineral phase mainly calcite, sodalite, quartz were soluble in acidic environment. As a result their rounded shapes of aggregate disappeared. On thermal treatment, porosity of the material was developed. The EDX spectra of ANRM shows the presence of Fe, O, Al, Ti, Si and C.

3.2. Effect of adsorbent dose, contact time, pH, and Adsorption kinetics

Batch study was conducted to find out the optimum adsorbent dose and the contact time for maximum possible removal of the adsorbate. A series of 50 mL samples of zinc having initial concentration 30 mg L^{-1} were shaken for 8 h with the varying adsorbent doses of 1–10 g L^{-1} . It was observed that the zinc removal efficiency was increased with increase of adsorbent dose and 0.2 $\text{g}/50 \text{ mL}$ of adsorbent could remove 99% of zinc. Thus, 0.2 $\text{g}/50 \text{ mL}$ was considered as

optimum dose and was used for further study. With the dose of 0.2 g/50 mL, the kinetic study was performed and it was observed that on 1 h of shaking 86% of total zinc could be removed. With further shaking for another 7 h the zinc removal reached at 99% (Fig. 4). Thus a shaking time of 8 h is adopted as equilibrium time. Adsorption of Zn(II) ions from multimetal solutions containing Zn(II), Pb(II), Cd(II) and organic matter (citric acid) was carried out at optimum conditions. It revealed that Zn(II) ions % removal capacity of ANRM was decreased to 96.04% at optimum conditions, mainly because of competitive effects of metal ions for adsorption sites.

The adsorptions of metal ions on the adsorbent strongly depend on the initial pH values of the solutions. Some experiments were carried out to examine the effect of initial pH on the adsorption of Zn(II) with initial concentration of 30 mg L⁻¹. The initial pH of the Zn(II) solution was adjusted from 3–9 using 0.1 M HCl or 0.1 M NaOH. The results show that the Zn(II) removal was favored at acidic pH 6, whereas adsorption was gradually decreases with increase of pH. Moreover, there is partial dissolution of red mud in the aqueous solution.

The rate constant K_1 for adsorption of Zn(II) was studied by Lagergren rate equation [15] for initial Zn(II) concentration of 30 mg L⁻¹.

Pseudo-first-order rate expression of Lagergren equation:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (2)$$

where q_e and q_t are the amount of Zn(II) adsorbed (mg g⁻¹) at equilibrium and at time t (min), respectively. K_1 is the adsorption rate constant of the pseudo-first-order adsorption (min⁻¹). The K_1 and correlation coefficient R^2 were calculated from the slope of the linear plot of $\log(q_e - q_t)$ versus 't' at different time intervals, are shown in Fig.5. The K_1 and R^2 were found to be 0.0068,

0.8885, Zn(II) which are low, indicating that the adsorption of Zn(II) onto ANRM did not follow Pseudo-first-order rate model.

The pseudo-second-order rate expression is [15]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where K_2 is the pseudo-second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). K_2 was calculated from the slope and intercept of the plot t/q_t versus t (Fig. 6). The values of K_2 , and R^2 were given in Table 1. The low value of K_2 and high value of R^2 indicates that the adsorptions followed pseudo-second-order kinetics.

3.3. Adsorption equilibrium isotherms

Commonly adsorption isotherm has been used to evaluate the adsorption capacity of an adsorbent for a particular adsorbate. The linearized Langmuir adsorption isotherm equation is valid for monolayer surface adsorption of adsorbate over a homogeneous adsorbent surface, and the adsorption of each molecule onto the surface has equal adsorption activation energy. The linearized Langmuir isotherm equation is as follows:

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \quad (4)$$

where C_e is the equilibrium concentration of adsorbate in solution (mg L^{-1}), q_e is the amount adsorbate adsorbed at equilibrium (mg g^{-1}), q_m is the theoretical maximum adsorption capacity (mg g^{-1}), and b is the Langmuir constant (L mg^{-1}). Figure 7 shows the linearized Langmuir isotherm plot of Zn(II) adsorption by ANRM at pH 6.0. It is observed that the Zn(II) adsorption is well fitted by Langmuir adsorption isotherm model with correlation coefficient $R^2 = 0.986$. This indicates a monolayer adsorption of Zn(II) onto the adsorbent surface. The maximum

adsorption capacity (q_m) of ANRM for Zn(II) was 14.92 mg g⁻¹ according to Langmuir model, which is better than that of previous research on adsorption of Zn(II) [10-12,16].

Freundlich adsorption isotherm assumes multilayer adsorption on heterogeneous surfaces.

Linearized form of the Freundlich isotherm equation is as follows:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)$$

where q_e is the amount of Zn(II) ions adsorbed at equilibrium time (mg g⁻¹), C_e is the equilibrium concentration of Zn(II) ions in the solution (mg/L), K_f is the adsorption capacity (mg g⁻¹), and n is an empirical parameter. The value of K_f , n , and R^2 were given in Table 2. Furthermore, the correlation coefficient of Langmuir isotherm is higher, so it fits the adsorption data better than the Freundlich isotherm.

In order to predict the adsorption efficiency of the adsorption process and to know whether the process is favorable or unfavorable for the Langmuir type adsorption, the dimensionless equilibrium parameter (r), can be calculated using the binding energy constant obtained from the Langmuir isotherm model as follows [17]:

$$r = \frac{1}{1 + bC_o} \quad (6)$$

where C_o is the initial Zn(II) concentration (mg/L) and b is the Langmuir constant (L mg⁻¹). From the magnitude of the r , the adsorption process can be described as $r > 1$ (unfavorable), $r = 1$ (linear), $0 < r < 1$ (favorable), $r = 0$ (irreversible). The calculated r values found in this study are between of 0.4197–0.0674 for 10–100 mg L⁻¹ concentration of Zn(II) adsorption onto ANRM, representing favorable adsorption process. Furthermore, the standard Gibbs free energy changes (ΔG°) for the adsorption process can be calculated by using the following equation:

$$\Delta G^\circ = -RT \ln b \quad (7)$$

where b (Table 2) is the Langmuir isothermal constant, R is universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the absolute temperature in K. The calculated ΔG° value is $-29.326 \text{ kJ mol}^{-1}$. The negative value of ΔG° indicates that the adsorption of Zn(II) on the ANRM was spontaneous under the experimental conditions.

4. Conclusions

In this study, thermally activated neutralized red mud was used as adsorbent for removal of Zn(II) from aqueous solutions. The adsorption kinetics was found to follow pseudo-second-order rate equation and equilibrates within 8 h. The maximum adsorption capacity of ANRM was 14.92 mg g^{-1} . This CO_2 -neutralized red mud can be used as low cost adsorbent for adsorption of Zn(II) from waste water.

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References

- [1] J. Ha, T.P. Trainor, F. Farges, G.E. Brown, Interaction of aqueous Zn(II) with hematite nanoparticles and microparticles part 1. EXAFS study of Zn(II) adsorption and precipitation, *Langmuir* 25 (2009) 5574–5585.
- [2] P. Trivedi, L. Axe, Modeling of Cd and Zn sorption to hydrous metal oxides, *Environ. Sci. Technol.* 34 (2000) 2215–2223.
- [3] H. Cesur, N. Balkaya, Zinc removal from aqueous solution using an industrial by-product phosphogypsum, *Chem. Eng. J.* 131 (2007) 203–208.

- [4] D. Mohan, K.P. Singh, Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse—an agricultural waste, *Water Res.* 36 (2002) 2304–2318.
- [5] H. Genc-Fuhrman, J.C. Tjell, D. McConchie, Increasing the arsenate adsorption capacity of neutralized red mud (Baxsol), *J. Colloid Interface Sci.* 271 (2004) 313–320.
- [6] S. Lofts, D.J. Spurgeon, C. Svendsen, E. Tipping, Deriving soil critical limits for Cu, Zn, Cd, and Pb: A method based on free ion concentrations, *Environ. Sci. Technol.* 38 (2004) 3623–3631.
- [7] S. Veli, B. Alyuz, Adsorption of copper and zinc from aqueous solutions by using natural clay, *J. Hazard. Mater.* 149 (2007) 226–233.
- [8] M. Sarkar, A.R. Sarkar, J.L. Goswami, Mathematical modeling for the evaluation of zinc removal efficiency on clay sorbent, *J. Hazard. Mater.* 149 (2007) 666–674.
- [9] M. Peld, K. Tonsuaadu, V. Bender, Sorption and desorption of Cd^{2+} and Zn^{2+} ions in apatite-aqueous systems, *Environ. Sci. Technol.* 38 (2004) 5626–5631.
- [10] V.K. Gupta, S. Sharma, Removal of cadmium and zinc from aqueous solutions using red mud, *Environ. Sci. Technol.* 36 (2002) 3612–3517.
- [11] E. Lombi, R.E. Hamon, S.P. Mcgrath, M.J. Mclaughlin, Lability of Cd, Cu, and Zn in polluted soils treatment with lime, beringite, and red mud and identification of a non-labile colloidal fraction of metals using isotopic techniques, *Environ. Sci. Technol.* 37 (2003) 979–984.
- [12] C. Brunori, C. Cremisini, P. Massanisso, V. Pinto, L. Torricelli, Reuse of a treated red mud bauxite waste: studies on environmental compatibility, *J. Hazard. Mater.* B117 (2005) 55–63.
- [13] ASTM D 1691–02, Standard Test Methods for Zinc in Water, Test Method A, 2007.
- [14] A.E. Greenberg, R.R. Trussell, L.S. Clesceri, Standard Methods for the Examination of Water and Wastewater, 16th ed., APHA, AWWA, WPCF, Washington, DC, 2005.

- [15] D.D. Do, Adsorption Analysis: Equilibrium and Kinetics, Imperial College Press, London, 1998.
- [16] S. Coruh, The removal of zinc ions by natural and conditioned clinoptilolites, Desalination 225 (2008) 41–57.
- [17] S.S. Tripathy, A.M. Raichur, Enhanced adsorption capacity of activated alumina by impregnation with alum for removal of As(V) from water, Chem. Eng. J. 138 (2008) 179–186.

List of Figures

Fig.1. Particle size distributions of red mud.

Fig.2. Thermogravimetric analysis and differential scanning calorimetry of neutralized red mud (NRM).

Fig.3. (a) SEM micrograph and (b) EDX spectrum of ANRM.

Fig.4. Time versus percentage removal of Zn(II).

Fig.5. Pseudo-first-order kinetics model for Zn(II) adsorption, time versus $\log (q_e - q_t)$ with initial Zn(II) concentration of 30 mg/L.

Fig.6. Pseudo-second-order kinetics model for Zn(II) adsorption at different initial solution pH.

Fig.7. Langmuir adsorption isotherm plot of $1/C_e$ versus $1/q_e$, Zn(II) adsorption on the ANRM.

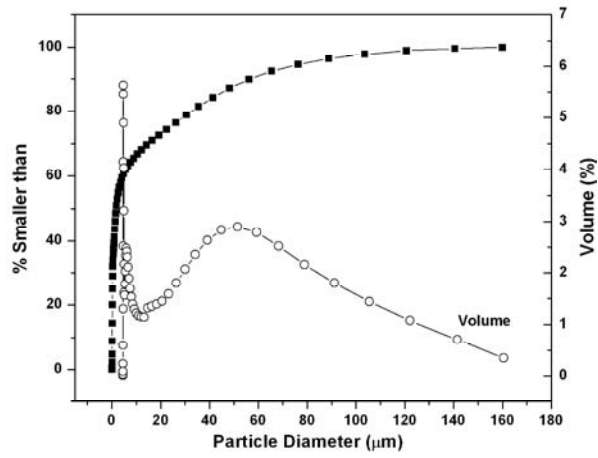


Fig. 1.

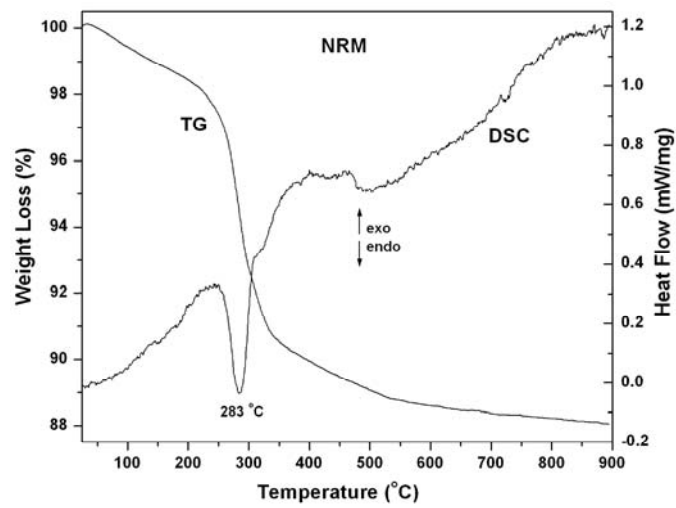


Fig.2.

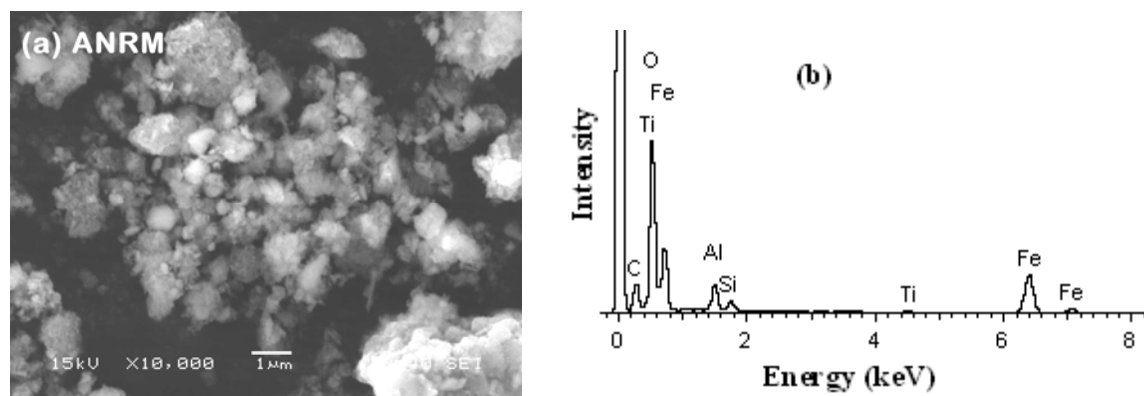


Fig.3.

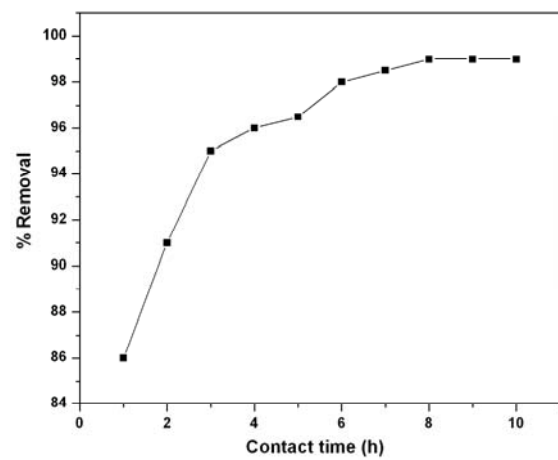


Fig.4.

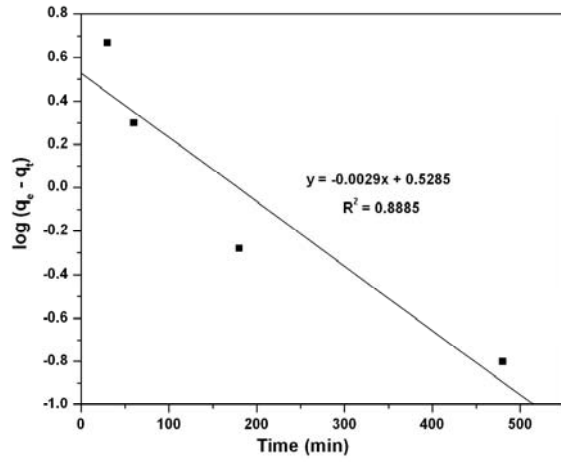


Fig.5.

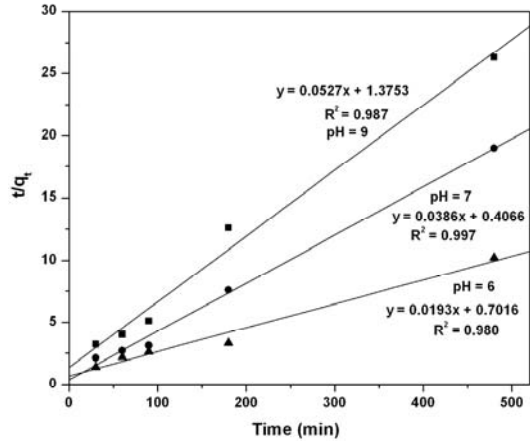


Fig.6.

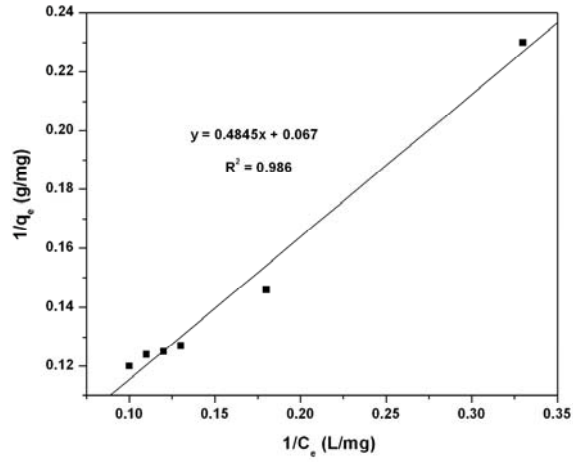


Fig. 7.

List of Table

Table 1: Pseudo-second-order kinetics constants and related regression coefficients

Table 2: Langmuir, Freundlich isotherms and Gibbs free energy

Table 1

Initial solution pH	q_e (mg g ⁻¹)	K_2 (g mg ⁻¹ min ⁻¹)	R^2
6	51.867	0.529×10^{-3}	0.980
7	25.859	3.677×10^{-3}	0.997
9	18.950	2.025×10^{-3}	0.987

Table 2

Langmuir isotherm		Freundlich isotherm		Gibbs free energy	
q_m	14.92 mg g ⁻¹	n	1.322		
b	0.138 L mg ⁻¹	K_f	3.174 mg g ⁻¹	ΔG°	-29.326 kJ mol ⁻¹
R^2	0.986	R^2	0.948		