



Research article

Equilibrium and kinetic studies of ferricyanide adsorption from aqueous solution by activated red mud

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ABSTRACT

In this study, activated red mud (ARM) was used as a new adsorbent for the removal of ferricyanide anions from aqueous solution. Based on the percentage of ferricyanide removal and ferricyanide adsorption capacity, optimum conditions were evaluated using the response surface method (RSM) and central composite design (CCD). In optimum conditions (pH = 5.6, adsorbent dosage of 2.59 g, ferricyanide concentration of 60 ppm and contact time of 60 min), the percentage of ferricyanide removal and ferricyanide adsorption capacity were obtained as 79.6% and 1.8 mg/g, respectively. The kinetics and equilibrium studies were evaluated by considering the effective parameters including pH and ferricyanide concentration. Kinetic studies were evaluated by kinetic models of pseudo first-order, pseudo-second-order (four different linearized forms), Elovich and intraparticle diffusion. The results of the kinetic study indicated that the mechanism of ferricyanide adsorption onto the ARM adsorbent is a chemisorption interaction by a fast ferricyanide adsorption onto ARM and subsequently the slow diffusion of ferricyanide ions into the ARM inner adsorption sites. The equilibrium studies showed that the adsorption process followed the Langmuir model in which ferricyanide adsorption onto ARM was homogeneous with monolayer adsorption. The results indicated that the activation process of red mud improved adsorbent efficiency and increased the adsorption capacity.

1. Introduction

Wastewaters are produced from industries including petrochemical (nylon, fibers, resins, metal plating, coke-processing plants and gold/silver extraction containing different amounts of both free and metal-complexed cyanides (Shifrin et al., 1996). Cyanide is used as a solvent for extraction of gold and silver ores and a flotation reagent for base metal recovery such as copper, lead and zinc in the mining industry (Dzombak et al., 2005; Kuyucak and Akcil, 2013; Logsdon et al., 1999). Some cyanide complexes are in a low toxicity level such as: soluble prussian blue ($KFe(III)[Fe(II)(CN)_6]$), and insoluble prussian blue ($Fe_4[Fe(CN)_6]_3$), ferricyanide [$Fe(III)(CN)_{3-6}$] and ferrocyanide [$Fe(II)(CN)_{4-6}$]. They will decompose slowly in case of exposure to light and release of free cyanide. They are extremely toxic for humans, the environment and aquatic organisms (Meeussen et al., 1992). Overall, cyanide is divided into three categories including: free cyanide such as hydrogen cyanide, strong metal cyanide complexes such as iron cyanide and weak acid dissociable cyanide compounds such as nickel and copper cyanide (Nsimba, 2009).

It is important to remove cyanide ions from wastewater before being discharged to the environment because of their harmful effect on

human health and the environment. Thus, some standards have been legislated for the discharge of cyanide bearing wastewaters by environmental agencies in many countries (Mudder and Botz, 2004; Donato et al., 2007). In recent years, cyanide removal from groundwater and wastewater is carried out by different technologies such as electrodialysis, reverse osmosis, alkaline-chlorination-oxidation, electrowinning, flotation, solvent extraction, acidification–volatilization–reneutralisation, hydrolysis–distillation, hydrogen peroxide, caro's acid, iron cyanide precipitation, activated carbons, resin and adsorption methods with various minerals (Young and Jordan, 1995; Dash et al., 2009; Botz, 2001).

Recently, different kinds of low-cost adsorbents were effectively used for removal ions such as soils, wastes and ore bearing minerals including ilmenite ($FeTiO_3$), hematite (Fe_2O_3), bauxite [$AlO.OH/Al(OH)_3$] and pyrite (FeS_2) (Dash et al., 2005; Young and Jordan, 1995). There are few studies about the iron-cyanide complex adsorptions onto soils and minerals. Noroozifar et al. (2009) used the modified natrolite zeolite–iron oxyhydroxide system as adsorbent for cyanide removal. They achieved a yield of 82% for removing cyanide at optimum conditions. The results indicated that the modified adsorbent can be effectively used to remove cyanide from industrial wastewaters

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(Noroozifar et al., 2009). Hanela et al. (2015) evaluated the removal of iron–cyanide complexes by combined UV–ozone and modified zeolite treatment (Hanela et al., 2015). They showed that this method achieved a significant iron–cyanide complex removal (66%). Gebresemati et al. (2017) investigated the optimization of cyanide sorption from aqueous medium by coffee husk using the response surface methodology. They obtained 90.6% cyanide adsorption in optimal conditions (initial concentration of 10 mg/L, contact time of 1 h, adsorbent dose of 1 g and pH of 8) (Gebresemati et al., 2017). Red mud (RM) is an industrial waste that is produced in large amounts as a consequence of caustic digestion of bauxite during alumina production (Brunori et al., 2005; Schwarz and Lalik, 2012). It has high alkalinity (pH of 10–12) that leads to serious environmental problems (Rai et al., 2012; Liu et al., 2011). The treatment of red mud due to the harmful environmental impacts of red mud and its enormous volume is necessary. This problem can be efficiently solved by conversion of the harmful red mud to useful products such as adsorbents. The high concentrations of oxides of aluminum, iron, titanium, silica and hydroxides in red mud make it appropriate as a cheap adsorbent for the removal of various ions from aqueous solution such as: dyes, phosphate, fluoride, chromium, arsenate, copper, zinc and nickel (Bhatnagar et al., 2011; Rai et al., 2012; Wang et al., 2005; Sutar et al., 2014).

The RM is a heterogeneous mixture of various minerals with different active sites. The monolayer coverage of adsorbate does not occur in the heterogeneous surface of the adsorbent. In this regard, the activation method of washing with HCl and then precipitating with ammoniac was applied to change and modify the heterogeneous surface of RM to the homogeneous surface. This facilitates the cost-effective removal of ferricyanide ions from the solution. In this study, the possibility of utilizing activated red mud as an adsorbent for cyanide removal from the solution was investigated. Initially, the effect of some operating parameters on the percentage of ferricyanide removal and ferricyanide adsorption capacity was evaluated. Then, the adsorption data for activated red mud was studied with different isotherm and kinetic equations in different pH and ferricyanide concentrations.

2. Experimental methods

2.1. Material and methods

Red mud samples of Jajarm mine, in north Khorasan province of Iran, were applied as adsorbent base material. The XRF studies show that the main chemical components of red mud are oxides of aluminum, calcium, iron, titanium and silicon. The XRD results showed that the primary red mud samples mainly contain hematite, sodalite, rutile, calcite, kaolinite, anatase, katoite, bohemite, cancrinite, hydroxalite and nushadir salt. In order to improve the reactivity of RM as adsorbent for removal of ions in the solution, activated red mud by ammonia was used (Deihimi et al., 2018). Potassium ferricyanide ($K_4Fe(CN)_6 \cdot 3H_2O$) and ammoniac (NH_3) were used in the study. The solution ionic strength was adjusted using KCl (1 M). Hydrogen chloride (HCl) and sodium hydroxide (NaOH) were used for adjusting the pH of the solution. All reagents were supplied from Merck. Experiments were carried out in the batch system in a 250 ml Erlenmeyer flask with a constant stirring rate of 160 rpm at a temperature of 298.15 K. The Erlenmeyer flask was covered by aluminum foil and sealed with rubber stoppers to prevent ferrocyanide decomposed by light. After equilibrium, the samples were centrifuged at 8000 rpm for 10 min and filtered to completely separate the liquid from solid phases. The ferricyanide percentage in the solution was determined by a UV–visible spectrophotometer at 420 nm (model HITACHI U-2000). Fourier transform infrared (FTIR) spectrometer at a spectral resolution of $+4\text{ cm}^{-1}$ (Nicolet 6700) and scanning electron microscopy coupled with energy dispersive X-ray (SEM/EDX) spectroscopy (FEI Quanta 200 electron microscopy (Holland)) were used to determine the nature of interactions and substrate characterization, respectively.

2.2. Adsorbent preparation

At first, RM was grinded and then sieved through a 100 mesh screen to obtain a grain size of less than 0.149 mm. In order to decrease the pH of RM (pH is usually greater than 13 for raw red mud), it was suspended in a solution of seawater with the weight ratio of liquid to solid of 3/1. This led to the precipitation of hydroxide, carbonate or hydroxy carbonate. Until reaching the equilibrium pH of 8–8.5, the solution was stirred for 1 h and then it took more than 1 h to sediment the mixture. After RM filtration by using Whatman filter paper No.42, it was kept in the oven overnight (100 °C) to completely dry up. Before using any activation method to obtain a uniform size of powder, the RM powder was sieved through a 0.149 mm screen. The sodalite compounds in the RM can block the available adsorption sites for ferricyanide adsorption. The acid treatment increases the adsorption capacity by leaching out of the sodalite compounds. Recently, activation of acid after neutralizing red mud has been efficacious to improve the physicochemical characters of red mud. In this regard, to increase the capacity of RM adsorption, the activation method of washing with HCl and then precipitating with ammoniac was examined.

In the preparation step, 5gr of red mud was refluxed in %20 wt HCl solution for 30 min. Then ammonia was added to complete precipitation until obtaining a pH range of 8–8.5. It is optimal to neutralize red mud until a pH of around 8–8.5 is obtained for a number of reasons including releasing chemically adsorbed Na, neutralizing alkaline buffer minerals and insolubility of toxic metals in this pH value. The BET results show that the BET of RM increased from 26.75 to 101.99 m^2/g after the activation method. The adsorbent special surface of ARM increased, creating high pores on its surface, and making it appropriate to adsorb more cyanide ions from the solution.

3. Results and discussion

3.1. Experimental design and optimization of parameters

In this study, the effect of the main variables including pH, adsorbent dosage, ferricyanide concentration and time (as independent variables) on the percentage of ferricyanide removal and ferricyanide adsorption capacity (as dependent variables) were investigated. In this regard, the response surface methodology based on a central composite design (CCD) was used by Design expert 10 (DX10) statistical software. Nineteen experiments were designed and randomly carried out to evaluate a relation between dependent variables and independent variables by the linear, two factor interaction, quadratic and cubic equations. Then, the analysis of variance (ANOVA) was used to determine the effective variables and their interaction on the output variables and the fitted model was evaluated (Gebresemati et al., 2017; Hoseinian et al., 2015; Sadeghalvad et al., 2016). The input and output variable ranges are presented in Table 1.

The ferricyanide removal percentage (R (%)) and ferricyanide adsorption capacity (q_e (mg/g)) are expressed as Eqs. (1) and (2), respectively:

$$R = ((C_i - C_e)/C_i) \times 100 \quad (1)$$

Table 1
The input and output variables range.

Factor	Name	Low Actual	High Actual	Mean	Standard deviation
A	pH	4.50	7.50	6	1.188
B	Adsorbent dosage (g)	1.20	4.50	2.850	1.307
C	Ferricyanide concentration (ppm)	60	160	110	39.603
D	Time (min)	15	60	40.533	24.387
Y1	R (%)	21.396	84.189	52.298	16.387
Y2	q (mg/g)	0.470	6.134	2.828	1.210

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