Amirkabir Journal of Civil Engineering

Amirkabir J. Civil. Eng., 51(2) (2019) 115-117

DOI: 10.22060/ceej.2018.13750.5469

Optimum condition determination of adsorption capacity and adsorption percentage of cyanide ions using activated red mud

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ABSTRACT: In this study, removal of ferrocyanide and ferricyanide ions from synthetic wastewater with activated red mud was studied. Two activation methods by ammonia (ABA) and cationic surfactant of cetyl trimethylammonium bromide (ABC) were used. In order to evaluate the process of cyanide ion adsorption and its effective parameters, 44 experiments were designed with seven variable factors using DX8 software by the response surface method. The results showed that the optimum conditions for achieving the highest adsorption capacity with ABC adsorbent were obtained as follows: pH=7.1, adsorbent dosage of 0.57 g, ferricyanide concentration of 126 ppm, contact time of 96.66 min, agitated speed of 120 rpm and ion strength of 0.24 M. In optimum conditions, the absorption capacity of 19.5 mg/g and the absorption percentage of 99.3% were obtained. The results showed that the use of ABC adsorbent has a higher efficiency in the removal of cyanide ions from the synthetic wastewater. Thermodynamic studies were carried out in optimal conditions. The results showed that the negative value of ΔG° parameters at different temperatures indicates the spontaneity of the cyanide complex adsorption process on adsorbents of ABA and ABC. The spontaneity of process increased with increasing the temperature.

Review History:

Received: 20 November 2017
Revised: 31 December 2017
Accepted: 3 January 2018
Available Online:17 January 2018

Keywords:

Adsorption
Cyanide, Red mud
CTAB
Thermodynamics

1- Introduction

Cyanide ions exist in the produced wastewaters from some industries which is extremely toxic for the humans, environment and aquatic organisms. Thus, the removal of cyanide before discharge to the environment is necessary [1]. Different techniques have been used in the literature for cyanide removal. Chemical and physical techniques are expensive, require special equipment and often problematic in terms of the environment [2]. In recent years, various environmentally compatible minerals have been used to remove cyanide from industrial wastewater. They have some advantages including abundant resources, low cost, easy to use and eco-friendly [3]. Red mud (RM) is an industrial waste with high alkalinity (pH of 10-12) that is produced as a consequence of caustic digestion of bauxite during alumina production. It has many Fe and Al oxides and hydroxides which can be used as a cheap adsorbent to remove of some ions from wastewater [4, 5].

In this study, the activated red mud with ammonia (ABA) and activated red mud with cetyltrimethylammonium bromide (ABC) were applied to remove the ferricyanide and ferrocyanide ions. In order to investigate the effective factors on the process, 44 tests were designed based on the surface-response method using DX8 software [6]. The pH, absorbent amount, absorbent type, ionic strength, stirring rate, time, adsorbate type and adsorbate dosage were considered as independent factors and the adsorption percentage and adsorption capacity as dependent factors. Then, thermodynamic studies were carried out in optimum obtained conditions from the experimental design.

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2- Material and method

In this study, the red mud of Jajarm alumina plant was used as adsorbent for removal of ferricyanide and ferrocyanide ions. The results of XRD show that RM mainly consists of oxides of aluminum, calcium, iron, silicon and titanium.

Cetyl trimethylammonium bromide (CTAB), potassium ferricyanide, potassium ferrocyanide and ammoniac were purchased from Merck. KCl for adjusting the solution ionic strength and HCl and NaOH for adjusting the solution pH was used. The percentage of cyanide ions was determined by a UV-visible spectrophotometer (model HITACHI U-2000) [7].

3- Preparation of activated red mud

RM was initially suspended in seawater solution (the weight ratio of liquid to solid was 3/1) and stirred for 1 hour to decrease the pH to 8-8.5 [8]. The RM was dried (at 100 ◦C) for 1 h and crushed to obtain the grain size of less than 0.149 mm. Then, the sample was examined by two activated methods of precipitating with ammoniac after acid washing and using CTAB surfactant [9]. In the method of precipitating with ammoniac after acid washing, 100 ml of HCl solution refluxes 5 gr of bauxsol during 30 minutes. Subsequently, ammonia was added to complete precipitation until obtaining a pH of 8-8.5. Then, the resulting solid samples were powdered and screened through the sieve of 0.149 mm. In the method of activation using CTAB surfactant, the appropriate amount of CTAB dissolved in 100 ml of distilled water. Then, 1% (w/v) CTAB solution was mixed with 20 g sample and stirred for 2 hours. After filtration of the solution, the solid phase was washed three times with distilled water to remove the negative effect of Br- ions and dried. AgNO3 was applied as the indicator for identification of Br- ions in the process.

4- Results and discussion

The results showed that the adsorbate dosage, absorbent amount and stirring rate have the higher effect on the adsorption of cyanide complexes on the adsorbents of ABA and ABC. The best adsorption capacity for ABA and ABC adsorbents was obtained at the high concentration of adsorbent (200 ppm) and the low amount of adsorbent (0.5 g). Interactions of pH and concentration on the removal percentage of ABA and ABC absorbents shows that removal percentage of cyanide complexes decreases with increasing of pH value. The pH changes the surface charge of activated RM. The zero charge point of the surface (pHzpc) is conceptually dependent on the chemical properties of the absorption surface. PHzpc is 5.5 for the ABA absorbent and 5-7 for the ABC absorbent. In the pH of lower than pHzpc, the cyanide anion complexes are adsorbed on the positive charge surface of adsorbent by hydroxyl group protonation. While, in the pH of higher than pHzpc, the absorption of the cyanide complexes is negligible due to the negative surface charge of adsorption with the hydroxyl group proteins. The adsorption percentage of the cyanide complexes at its highest concentration were obtained 54% and 90% on the ABA absorbent at pH 5-7 and on the ABC absorbent at pH 5.5, respectively. The interaction of time and adsorbate dosage shows that the adsorption percentage increases with increasing simultaneously of these two parameters.

Figure 1 shows the effect of adsorbent type on adsorption capacity and adsorption percentage. The results indicate that ABC adsorbent has a higher efficiency than ABA in the removal of cyanide ions from synthetic wastewater. The optimum conditions of ABC adsorbent to achieve the highest adsorption capacity were pH=7.1, adsorbent dosage of 0.57 g, ferricyanide concentration of 126 ppm, contact time of 96.66 min, agitated speed of 120 rpm and ion strength of 0.24 M. FTIR spectra for ABA and ABC absorbents before and after adsorption of cyanide ions are shown in figure 2. A new bond is observed at 2056 cm-1 after absorption of ferrocyanide, which indicates the absorption of ferricyanide on the absorbents. The ferricyanide absorption peak on the ABC absorbent surface is greater than that of the ABA absorbent, which indicates better adsorption of ABC [10].

The absorption thermodynamic study was investigated in optimal obtained conditions from the experiment design. The results showed that the cyanide complex adsorption process on adsorbents of ABA and ABC are spontaneity and increased with increasing the temperature.

5- Conclusions

In this study, two types of activated red mud (ABA and ABC) have been utilized as ferricyanide and ferrocyanide adsorbent. The optimal condition for the adsorption percentage and adsorption capacity of ferricynide and ferrocynide ions from synthetic wastewater were evaluated using DX8 with considering effective factors of the pH, absorbent amount, absorbent type, ionic strength, stirring rate, time, adsorbate type and adsorbate dosage. The results showed that the ABC adsorbent has a higher efficiency than ABA adsorbent. The absorption thermodynamic study indicated the cyanide complex adsorption process are spontaneity.

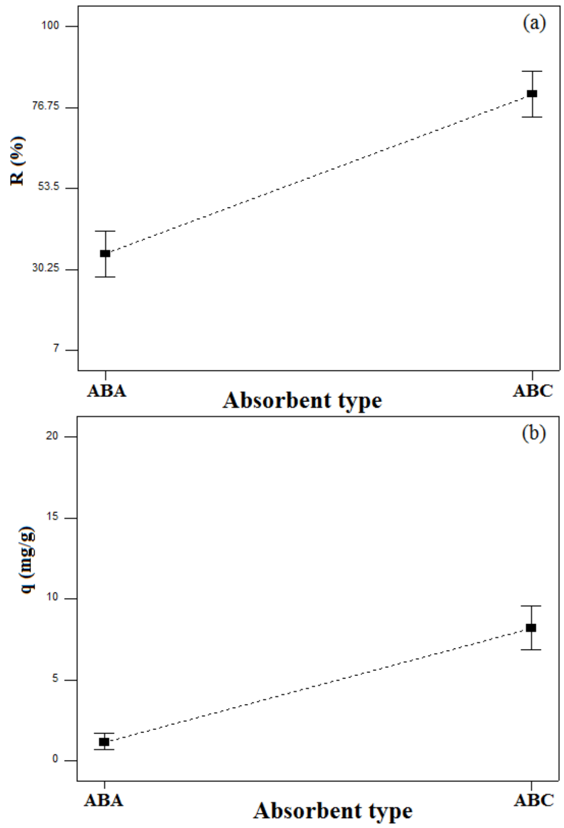

Figure 1. The effect of absorbent types of ABA and ABC on the a) adsorption capacity and b) removal present of ferrocyanide- and ferricyanide

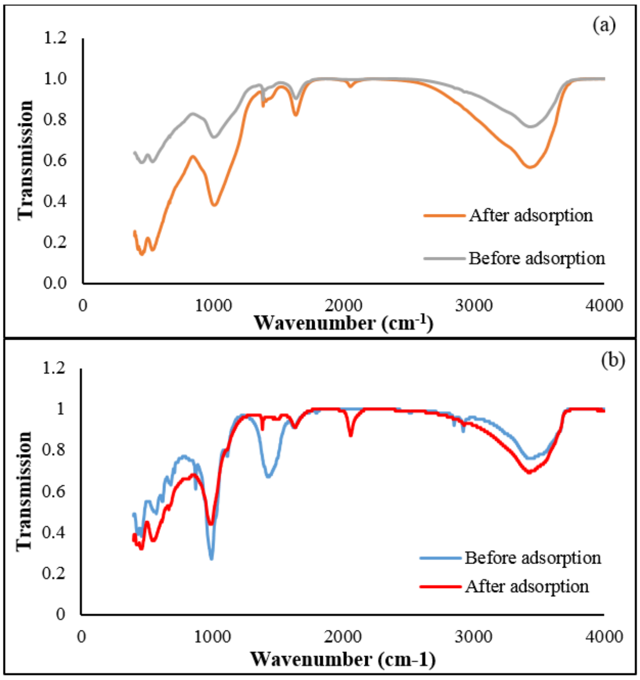

Figure 2. FTIR analysis of a) ABA and b) ABC, before and after adsorption of cyanide ions

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Please cite this article using:

N.Deihimi ,M.Irannajad ,B.Rezai,Optimum condition determination of adsorption capacity and adsorption percentage of cyanide ions using activated red mud ,*Amirkabir J. Civil Eng.*, 51(2)(2019)377-387.

DOI: 10.22060/ceej.2018.13750.5469