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Optimization of Effective Parameters for Cd (II) Removal from Aqueous Solutions by Red Mud Using Design of Experimental (Box-Behnken)

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ABSTRACT

The objective of this study is to remove the Cd (II) from aqueous solution by using the red mud in batch adsorption methods. The adsorption process has many advantages such as: low cost of adsorbent, utilization of domestic waste as adsorbents and environmentally friendly. The parameters such as: red mud dosage, contact time and pH by Box-Behnken designs optimized and their effects on removal percentage were investigated. The present study showed that pH is important factor in removal process. Cadmium solutions were quantitatively determined using an atomic absorption spectrophotometer (AAS). The equilibrium adsorption of the Cd^{2+} was tested with the popular adsorption isotherms, Langmuir and Freundlich models. The adsorption capacity of adsorbent for Cd^{2+} is more than 13 mg/g. The Langmuir adsorption isotherm model matches the experimental data well ($R^2 \geq 0.98$).

KEYWORDS: Adsorbtion methods, Red mud, Box-Behnken designs, Equilibrium isotherm.

1. INTRODUCTION

The increase of industrial activities has intensified environmental pollution problems and the deterioration of several aquatic ecosystems with the accumulation of heavy metals in world [1].

Heavy metal species are some of the most common pollutants that are found in industrial wastewaters because of their toxicity, these species can have a serious impact if released into the environment as a result of bioaccumulation and they may be extremely toxic even in trace quantities [2].

Cadmium is used in the steel industry and in plastics and also its compounds are widely used in batteries. Cadmium is released to the environment in wastewater, and diffuse pollution is caused by contamination from fertilizers and local air pollution. Contamination in drinking-water may also be caused by impurities in the zinc of galvanized pipes and solders and some metal fittings. Food is the main source of daily exposure to cadmium and Smoking is a significant additional source of it. Cadmium is characterized as 'heavy metals' because it have an atomic density of ≥ 6 g/cm-3. Cadmium is particularly toxic as a comparatively small dosage can be harmful to human health. The 1958 WHO International Standards for Drinking-water did not refer to cadmium. The 1963 International Standards recommended a maximum allowable concentration of 0.01 mg/lit, based on health concerns. This value was retained in the 1971 International Standards as a tentative upper concentration limit, based on the lowest concentration that could be conveniently measured. In the first edition of the Guidelines for Drinking-water Quality, published in 1984, a guideline value of 0.005 mg/lit was recommended for cadmium in drinking-water [3-5].

There are various physical and chemical methods for cadmium removal used to industrial effluents containing Cd (II). Those methods can be broadly divided into the following categories: chemical methods, membrane, ion exchange, solvent extraction and adsorption techniques. Conventional techniques have their own inherent limitations such as less efficiency, sensitive operating conditions, production of secondary sludges and costly for their disposal. Another powerful technique for heavy and toxic ions remediation is adsorption. The adsorption process has many advantages such as: low cost of adsorbent, easy availability, utilization of industrial, biological and domestic waste as adsorbents, low operational cost, ease of operation compared to other processes, reuse of adsorbent after regeneration, capacity of removing heavy metal ions over wide range of pH and to a much lower level, ability to remove complex form of metals that is generally not possibly by other methods, environmentally friendly, cost effective and technically feasible alternative due to utilization of biomaterials. The last few decades have witnessed tremendous interest in development of new adsorbents to modify the performance of purification processes [6].

Red mud is generated as a waste during the processing of bauxite, the most common ore of aluminum. Bauxite was discovered by P. Berthier in 1821 in southern France and more than 68 years later, in 1889, Karl Josef Bayer invented the Bayer process for the production of alumina from bauxite [7]. Red mud has been documented well that it can be used as a low cost absorbent for removing heavy metal ions, such as Pb^{2+}[8], Zn^{2+} [9], Cu^{2+} [10] and other compound such as phenol [11], colors [12-13], phosphate [14], and having high adsorption capacity for cadmium removal after specific thermal [15] or chemical pretreatment [16-17].

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However, most of the earlier works pertaining to utilization of red mud employed was only powdered red mud. Powdered red mud, though endowed with a high specific adsorption area, it is not suitable for large scale commercial operation because it requires filtration for removal of the adsorbent [18].

Apak et al. reported that the toxic heavy metals, i.e. copper (II), lead (II) and cadmium (II), can be removed from water by metallurgical solid wastes, i.e. bauxite waste red mud and coal fly ashes acting as adsorbents. Both adsorption studies and column studies were carried out to optimize the adsorption process. The adsorption data were analyzed and fitted to linearized adsorption isotherms [19]. Granular red mud (GRM) was evaluated for its potential to remove cadmium ions from aqueous solutions as a low-cost adsorbent. Kinetics data at initial pH 6.0 and 3.0 were fitted to pseudo-second-order model. The maximum adsorption capacities for GRM observed in the experiments were determined as 38.2 mg/g at 20$^{\circ C}$, 43.4 mg/g at 30$^{\circ C}$ and 52.1 mg/g at 40$^{\circ C}$ [16]. The feasibility of red mud (RM) was assessed for wastewater treatment using batch method by Lopez et al. The aggregates were prepared using red mud and 8% (w/w) $CaSO_4$ and examined their potential by batch and column experiments. The RM aggregates showed maximum adsorption capacities for Cu(II), Zn(II), Ni(II) and Cd(II) of 19.72, 12.59, 10.95 and 10.57 mg/g, respectively with contact time of 48h [20]. Some authors also examined red mud for the removal of cadmium and zinc from aqueous solutions. The removal of Cd(II) and Zn(II) was almost complete at low concentrations [21]. Adsorption experiments of heavy metal ions i.e., Pb(II), Cu(II), Cd(II) in aqueous solutions by the pellet-type red mud adsorbents were studied under various experimental conditions. It was found that the pellets made from a mixture of 58.7 wt% red mud, 25.2 wt% kaolin, 11.7wt% sodium silicate solution, 2.9 wt% fly ash, and 1.5 wt% magnesium chloride at 600$^{\circ C}$ exhibited the highest removal efficiency of the heavy metal ions [22]. Red mud has also been studied as a potential adsorbent for the removal of toxic bivalent cations i.e., Cd(II), Zn(II), Cu(II) and Pb(II) from aqueous solutions in the presence of 0.01M $NaNO_3$[23].

In the present work, parameters such as adsorbent dosage, contact time, and pH and their influence on the removal percent was studied. The optimum amount could be either a maximum or a minimum of a function of the design parameters. One of methodologies for obtaining the optimum is response surface technique.

It is essential that experimental design methodology is a very economical way for extracting the maximum amount of complex information, a significant experimental time saving factor and moreover, it saves the material used for analyses and personal costs as well [24]. Box-Behnken designs are a type of response surface method, which provides detailed information about the solution space, allowing researchers to better understand the forces affecting the output of the model.

The aim of this study was removal of cadmium from water with red mud as an adsorbent. We have used Box-Behnken method to obtain optimal parameters.

2. EXPERIMENTAL

2.1. Absorbent

Red mud, the solid waste used as sorbent was supplied from Jajarm Aluminum Plant, Iran. For preparing of red mud it thoroughly washed with distilled water, dried in 110 °C for 48 h in oven and sieved with 60 mesh screen.

2.2. Chemicals and reagents

All chemicals and reagents were analytical grade and used without further purifications. The metal ion stock solution with a concentration of 1000 mg/L was prepared from high purity nitrate salts of cadmium. The metal ion solution was subsequently diluted with deionized water until 10 ml volume to obtain desired concentration ranging from 40 mg/L. The pH adjusted was done with ammonium solution.

2.3. Instrumentation

In order to obtain the characterization of adsorbent, Qualitative and semiquantitative analysis was carried out by X-ray fluorescence (XRF) (Philips model Magix Pro) and X-ray diffraction (XRD) (Siemens model D500).Cadmium solutions were quantitatively determined using an atomic absorption spectrophotometer (AAS) (Shimadzu model AA611). pH measurements were made using a pH meter equipped with a combine electrode (Model Metrohm No. 827).

2.4. Batch adsorption

Batch adsorption was performed under controlled experimental conditions at a desired red mud dosage, contact time and pH. In order to ensure sufficient interaction between Cd^{2+} and red mud adsorbent, the speed of the stirrer was kept at 750 rpm for all the batch experiments at room temperature (25 ± 0.1°C). After centrifugation, the solution was filtered directly. The filtrate was analyzed using an atomic absorption spectrophotometer.

The adsorption capacity of Cd(II) ions by red mud were calculated by the following mass balance equation:

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

Where C_o and C_e are the initial and final (equilibrium) concentrations of the metal ion in solution (mg/L), Vis the solution volume (L) and m is the mass of sorbent (g).

3. RESULT AND DISCUSSION

3.1. Characterization of adsorbent

3.1.1. XRF analysis

The major constituents of the red mud used in experiments were (mass fraction, %): Fe_2O_3, 28.41; Al_2O_3, 17.27; TiO_2, 7.36; SiO, 19.29 and CaO, 21.35. Meanwhile, the all mineral compositions of the red mud are listed in Table 1.

Table 1. All mineral compositions of red mud (mass fraction, %)

Composition	% by wt	Composition	% by wt
Na_2O	1.79	Sc_2O_3	600*
MgO	1.75	TiO_2	7.36
Al_2O_3	17.25	Cr_2O_3	0.40
SiO_2	19.29	Fe_2O_3	28.41
SO_3	1.20	Sr	0.11
Cl	0.14	Zn	300*
K_2O	0.37	ZrO_2	0.19
CaO	21.35	Nb_2O_5	300*

*Scale in ppm unit

3.1.2. XRD analysis

According to the XRD data (Fig. 1), the red mud contains mainly hematite [Fe_2O_3], calcite [$CaCO_3$], katoite [$Ca_3Al_2(SiO_4)(OH)_8$]. Anatase [TiO_2], kaolinite [$Al_2Si_2O_5(OH)_4$] and cancrinite [$Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2.2H_2O$] are also present as minor constituents.

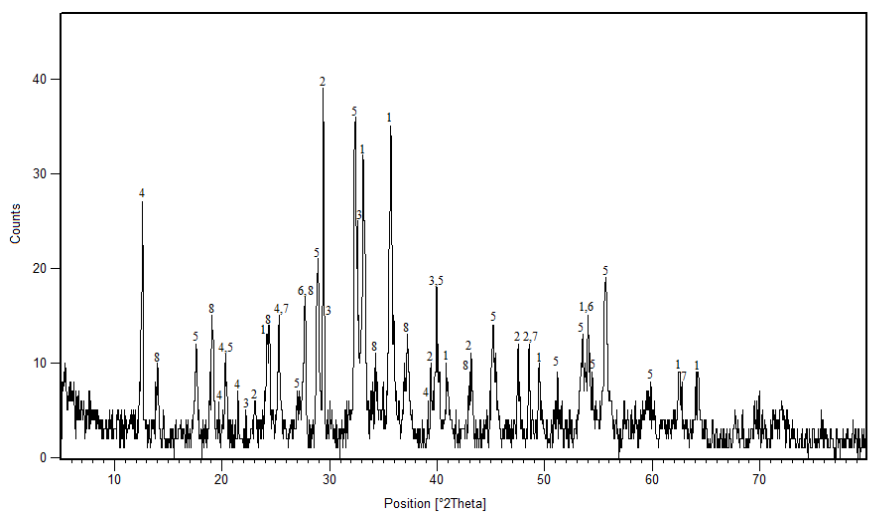

Fig. 1. XRD diagram of red mud used. 1, hematite; 2, calcite; 3, sodium calcium silicon oxide; 4, kaolinite; 5, katoite; 6, rutile; 7, Anatase; 8, cancrinite.

3.2. Optimization procedure by Box-Behnken design

In order to exact optimization of the removal condition and also to study the possible interaction between the parameters, Box-Behnken design was applied. For the removal of Cd (II) by the proposed method, levels of the parameters were selected based on the result obtained from the initial experiments. Based on Box-Behnken design, 15 experiments were required to obtain the response surface. The experimental runs and the observed response for the mentioned 15 experiments according to the three-factor and three-levels are given in Tables 2, 3.

Table 2. Variables in Box-Behnken design

Factor	Key	Levels			Unit
		–	0	+	
Dosage	A	0.025	0.0625	0.1	g
Time	B	1	15.5	30	min
pH	C	2	7	12	–

Table 3. Matrix in Box-Behnken design and result for each experimental

Experimental code	A	B	C	Response (removal %)
1	–	0	–	29.19
2	0	0	0	83.48
3	0	+	+	100.00
4	–	+	0	52.79
5	+	+	0	84.07
6	–	0	+	98.82
7	0	0	0	78.17
8	0	–	+	99.41
9	0	–	–	32.14
10	+	–	0	79.35
11	+	0	–	74.04
12	0	+	–	37.45
13	–	–	0	40.40
14	+	0	+	98.82
15	0	0	0	74.04

3.3. Effect of on adsorbent

The effect of red mud dosage on removal percent at different initial pH of Cd^{2+} solution (2, 7 and 12), using contact time dosage of 15.5min, shows in Fig 2. It can be seen in pH 7 and 2 that as the red mud dosage increases, the removal rate of Cd^{2+} also increases. However, the removal percentage was unchanged in pH=12.

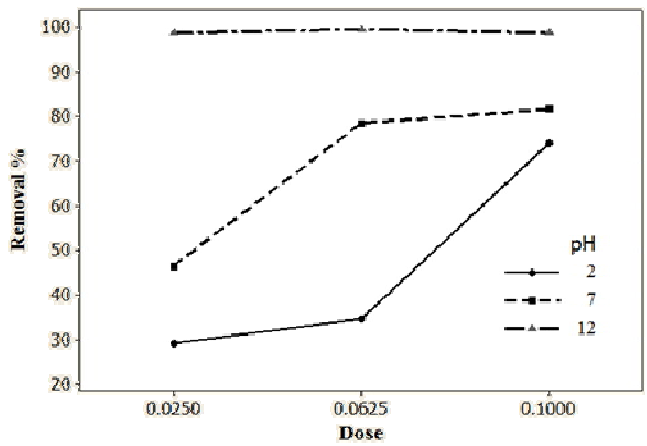

Fig. 2. Effect of red mud dosage on removal percent at different initial pH of Cd^{2+} solution

3.4. Effect of contact time on adsorption

The effect of contact time on adsorption rate at different initial pH of Cd^{2+} solution, using adsorbent dosage of 0.0625 g are presented in Fig 3.

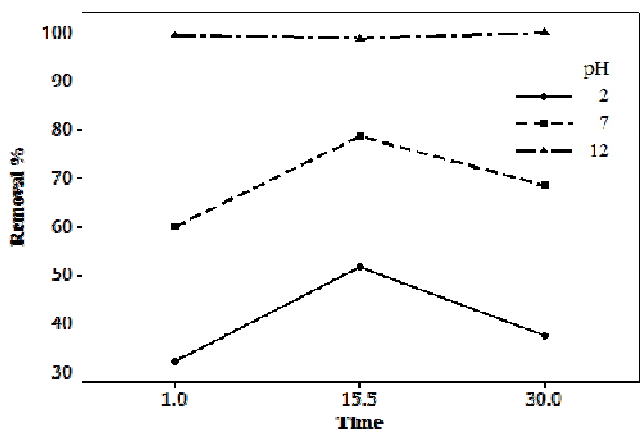

Fig. 3. Effect of contact time on adsorption rate at different initial pH of Cd^{2+} solution

As it shown in Fig. 3 as the contact time increases, the removal rate of Cd^{2+} also increases until about 15.5 min and thereafter decreases in pH 2 and 7.At all of time (1.0, 15.5 and 30 min) was observed highest of removal amount in pH 12.

3.5. Effect of pH on adsorption

It can be seen from Figures 2 and 3, that is always highest of removal percentage in pH=12.

When hold values pH 12, Common effect of contact time and adsorbent on the removal percentage is shown in Fig 4.

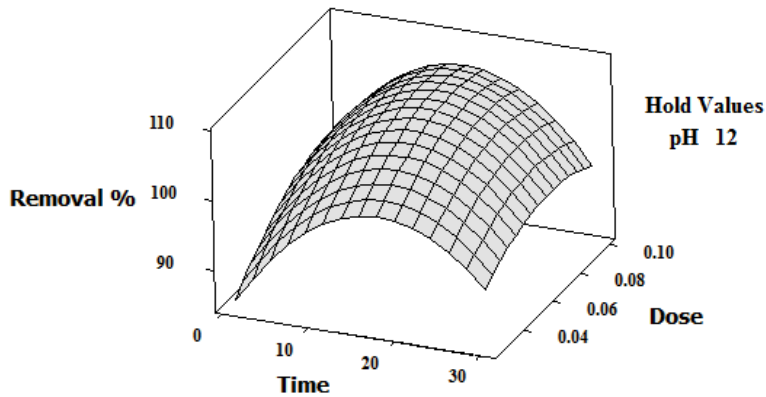

Fig. 4. Effect of contact time and adsorbent on the removal percentage at hold values pH=12

3.6. Adsorption isotherm and kinetics

The equilibrium adsorption of the Cd^{2+} was tested with the popular adsorption isotherms, Langmuir and Freundlich models. The Langmuir equation is expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \tag{2}$$

Where C_e is the concentration of Cd (II) (mg/L) at equilibrium, q_{max} is the monolayer capacity of the adsorbent (mg/g) and b is the Langmuir adsorption constant (L/mg).

Freundlich isotherm is the semiempirical equation, with the assumption of multilayer absorption. Theequation is expressed as:

$$q_e = kC_e^{\frac{1}{n}} \tag{3}$$

Where C_e is equilibrium concentration, k is the sorption capacity(mg/g) and n is an empirical parameter.

Langmuir and Freundlich models are the simplest and most commonly used isotherms to represent the adsorption of components from a liquid phase onto a solid phase. The graphical comparison of the experimental value with the calculated value from the Freundlich and Langmuir isotherms for cadmium adsorption by red mud adsorbent is shown in Figures 5,6.

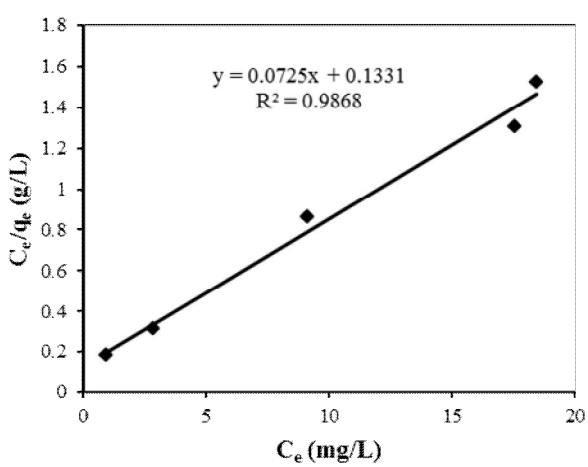

Fig. 5. Langmuir adsorption isotherm for Cd^{2+} onto red mud at different concentration

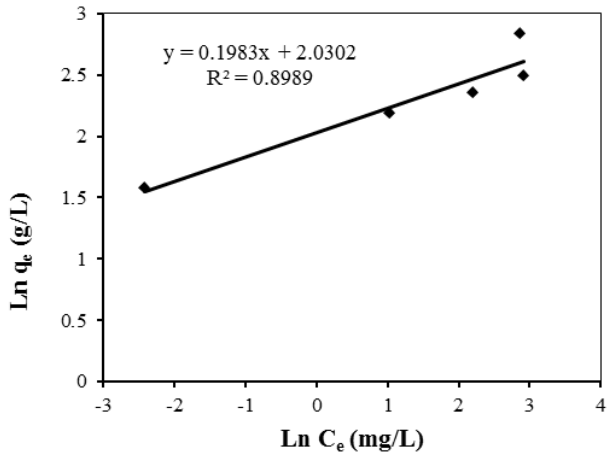

Fig. 6. Freundlich adsorption isotherm for Cd^{2+} onto red mud at different concentration

The R^2 value in Figures 5,6 clearly indicates that the Langmuir mode fits better than the Freundlich model. The value of q_{max} indicates the monolayer adsorption capacity of the red mud, which increases with the increase of the pH during the adsorption process.

4. Conclusions

1) There are various physical and chemical methods for cadmium removal that adsorption process has many advantages such as: low cost of adsorbent, easy availability, utilization of domestic waste as adsorbents, reuse of adsorbent after regeneration, capacity of removing heavy metal ions over wide range of pH and to a much lower level, environmentally friendly.

2) In investigating the possibility of usage of solid wastes as cost-effective sorbents in toxic heavy metal (Pb, Cd, and Cu) removal from contaminated water, red muds have been shown to exhibit a high capacity.

3) The present study showed that pH has highest impact on removal percentage and the optimized parameters that obtained from Box-Behnken design for dosage adsorbent, contact time and pH were 0.08 g, 15.93 min and 12 respectively.

4) The Langmuir adsorption isotherm model matches the experimental adsorption isotherm better. The adsorption capacity of adsorbent for Cd^{2+} is more than 13 mg/g. R^2 values are more than 0.98.

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