

*Full Length Research Paper*

# Removal of cobalt (II) ions from aqueous solution by using alternative adsorbent industrial red mud waste material

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**This study on the removal of cobalt ions from aqueous solutions by red mud was conducted in batch condition. Its objective was to investigate the possibility of using red mud waste material as an alternative to high cost commercial adsorbent materials for the removal of cobalt from aqueous solution. In this study, batch experiments were carried out for the adsorption of cobalt onto red mud industry waste. The red mud waste material was successfully used for the removal of cobalt ion from aqueous solution and the technique appears industrially applicable and viable. The potential of economically cheap waste materials like red mud was assessed for cobalt adsorption from aqueous solutions. The operating variables studied were contact time, initial solution pH, initial metal concentration, temperature and adsorbent dosage. The experimental investigation results show that activated red mud has a high level of adsorption capacity for cobalt ion. The adsorption data was correlated with the Langmuir and Freundlich isotherm models. It was found out that the Langmuir and Freundlich isotherms fitted well to the data. Consequently, it was concluded that the red mud can be successfully used for the removal of the cobalt ions from the aqueous solutions with heavy metals.**

**Key words:** Red mud, cobalt removal, aqueous solution, adsorption isotherms.

## INTRODUCTION

Environmental contamination with metal ions represents a potential treat to human, animals and plants. The metal ions do not undergo biodegradation and many of them are soluble in aqueous solutions, therefore, become more available for living systems and accumulate in the environment. Due to rapid development and industrialization in many countries, the levels of industrial pollution have been rising, steadily. So, the pollution problem of industrial wastewater is becoming more and more serious in the world. Consequently, the treatment of polluted industrial wastewater remain a topic of global concern since wastewater collected from municipalities, communities and industries must ultimately be returned

to receiving waters or to the land (Hashem, 2007; Caramalau et al., 2009).

Cobalt compounds are essential in many industries. Their applications in nuclear power plants, metallurgy, mining, pigments, paints and electronic are only few examples where the presence of cobalt in waste waters represents a major environmental problem (Baun and Christensen, 2004; Caramalau et al., 2009). Moreover, contamination of ground water is another major concern in the management of water resources. Contaminants, such as heavy metals arise from wide variety of processes occurring in the soil, including diffusion, mechanical dispersion, chemical reaction, decay, adsorption and biodegradation. The presence of heavy metal has a potentially damaging effect on human physiology and other biological systems when the tolerance levels are exceeded. They remain a serious public health problem to human health. With

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increasing environmental awareness and legal constraints imposed on discharge of effluents, the need for cost-effective alternative technologies is essential for removal of heavy metals from industrial wastewater (Khouider et al., 2004; Adesola et al., 2006; Egila et al., 2010).

The permissible limits of cobalt in the irrigation water and livestock wastewater are 0.05 and 1.0 mg/L, respectively (Environmental Bureau of Investigation, Canadian Water Quality Guidelines) (Rengaraj and Moon, 2002). The acute cobalt poisoning in humans may cause serious health effects, e.g. asthma like allergy, damage to the heart, causing heart failure, damage to the thyroid and liver. Cobalt may cause mutations (genetic changes) in living cells. Exposure to ionizing radiation is associated with an increased risk of developing cancer. With a better awareness of the problems associated with cobalt, research studies related to the methods of removing cobalt from wastewater have drawn attention, increasingly. Although, a number of physico-chemical technologies are available for the metals removal, the costs associated with some technologies or their ineffectiveness, have resulted in industrial waste adsorbent being considered as an alternative technology for trace metal removal (Bhatnagar et al., 2010).

The sorption studies of cobalt are essential for nuclear and hazardous waste management. Different inorganic and organic sorbents have been considered for cobalt immobilization. Inorganic exchangers have interesting properties, such as resistance to decomposition in the presence of ionizing radiation or at high temperatures, which have made them interesting for the treatment of nuclear waste (Demirbag, 2003; Yavuz et al., 2003; Vijayaraghavan et al., 2005).

Solid wastes are generally used as adsorbent for the removal of heavy metal from wastewater. One type of solid waste materials, red mud, is largely produced from the alumina industry. Red mud emerges as a by-product of the caustic leaching of bauxite to produce alumina. This waste material has a reddish-brown color and a superfine particle size distribution. Alkalis, iron oxides and hydroxides, aluminum hydroxides, calcium carbonate, titanium and silica form its chemical composition. Red mud is principally composed of fine particles of silica, aluminum, iron, calcium and titanium oxides, and hydroxides, which are responsible for its high surface reactivity (Chvedov et al., 2001; Kalkan, 2006). Because of these characteristics, red mud has been the subject of many investigations, including some on the removal of toxic heavy metals from wastewater and acid mine drainage or on reducing the leaching of soil nutrients (Apak et al., 1998; Lopez et al., 1998; Gupta et al., 2004; Kalkan, 2006; Wang et al., 2008). It has been noted in the literature that the red mud could be used for decontaminating mining sites and other contaminated areas, which generate acidic leachates and produce high concentrations of hazardous heavy metal ions

(Komnitsas et al., 2004). The investigation showed that red mud is a very valuable material for the removal of copper ions from aqueous solutions with heavy metals (Nadaroglu et al., 2010).

The aim of this study was to examine the efficiency of industrial red mud by-products as adsorbent and the optimization of parameters for the removal of cobalt from aqueous solutions. The adsorption of cobalt ion on red mud was investigated as a function of contact time, pH, initial metal concentration, temperature and adsorbent dose. The equilibrium data was described by the Langmuir and Freundlich adsorption isotherms.

## MATERIALS AND METHODS

### Red mud

Red mud by-products used in this study was supplied from the Seydisehir Aluminum Plant (Konya, Turkey). Red mud is produced during the Bayer process for alumina production. Bauxite ores are usually a mixture of minerals rich in hydrated aluminum oxides. However, they also contain iron, silicon and titanium minerals. After the digestion of bauxite ores with sodium hydroxide at elevated temperature and pressure, aluminum oxide is dissolved in the solution and the solid residue is red mud. In general, red mud is a very fine material in terms of particle size distribution, having an average particle size  $<10 \mu\text{m}$ . Typical values would account for 90% value below  $75 \mu\text{m}$ . Its engineering properties are given as shown in Table 1. Chemical composition of the red mud used in the tests was analyzed by means of an Atomscan 25 inductively coupled plasma (ICP) spectrophotometer of Thermo Jarrell Ash. Results are as shown in Table 2. The major component is iron oxide, followed by alumina and silica. The red mud composition is strongly dependent on the characteristics of precursor bauxite ore, as well as on applied technological process, and consequently fluctuates strongly between samples generated in different parts of the world. The quantity of each major constituent of investigated sample falls into ranges mentioned in the literature (Wang et al., 2008; Smiljanic et al., 2010). Red mud contains many residual minerals from bauxite, such as sodalite, cancrite, hematite, rutile, diaspore and calcite (Table 3).

The alkaline red mud was thoroughly washed with distilled water until it became neutral. The suspension was wet sieved through a 200 mesh screen. A little amount of the suspension remained on the sieve and was discarded. The solid fraction was washed five times with distilled water following the sequence of mixing, settling and decanting. The last suspension was filtered, and the residual solid was then dried at  $105^\circ\text{C}$ , ground in a mortar, and sieved through a 200 mesh sieve. After red mud was washed with distilled water, acid pretreatment was carried out by boiling 100 g of red mud. Then, it was washed with distilled water, filtered and dried. This adsorbent was used in this research.

### Analysis methods

For studying metal adsorption, 1 g of red mud as adsorbent was taken and it was then suspended in 30 ml of 1 mg/ml  $\text{CoCl}_2$ , at pH between 2 and 9 and contacted batchwise in a thermostatic ( $t = 30 \pm 0.1^\circ\text{C}$ ) water-bath agitator for 1 h to enable equilibration of the sorbent and solution phases. For studying cobalt determination, 1 ml of sample solution containing preferably  $2.0 \times 10^{-5}$  to  $4.0 \times 10^{-4}$  mmol (1 to 24  $\mu\text{g}$ ) cobalt was taken; 1 ml of  $0.8 \times 10^{-3}$  M dithizone solution (20-fold of maximum amount of cobalt) followed by 1 ml of

**Table 1.** Engineering properties of red mud used in the study.

Property	Value
Bulk density (mg/m <sup>3</sup> )	14.30
Specific surface area (m <sup>2</sup> /g)	10 - 25
Specific gravity	3.05
Porosity	0.56
pH	12 - 13

**Table 2.** Chemical compositions of red mud used in the study.

	Constituent (%)	
	Before treatment	After treatment
SiO <sub>2</sub>	17.29	19.40
Al <sub>2</sub> O <sub>3</sub>	20.20	22.40
Fe <sub>2</sub> O <sub>3</sub>	35.04	37.20
CaO	5.30	5.87
MgO	0.33	0.22
TiO <sub>2</sub>	4.00	5.20
Na <sub>2</sub> O	9.40	8.20
Heat loss	8.44	1.51

**Table 3.** Mineralogical composition of red mud used in the study.

Mineral (%)	
Sodalite (Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·1.68 SiO <sub>2</sub> ·1.73 H <sub>2</sub> O)	32.20
Cancrite (3NaAlSiO <sub>4</sub> NaOH)	27.60
Hematite (Fe <sub>2</sub> O <sub>3</sub> )	34.70
Rutile (TiO <sub>2</sub> )	1.60
Diaspore (AlO(OH))	2.60
Calcite (CaCO <sub>3</sub> )	1.30

distilled water and 1 ml of concentrated NH<sub>3</sub> solution were added to yield a final volume of 4 ml (Ozturk et al., 2000). After 1 mM dithiozone and 1 ml distilled water prepared in the 0.5 ml, 0.1 M KH<sub>2</sub>PO<sub>4</sub> (pH:12) buffer solution were added to 0.5 ml of the sample taken from testing solution media, and was incubated. The amount of cobalt ions adsorbed was calculated as;

$$q_e = [(C_o - C_e)V]/m \quad (1)$$

where  $q_e$  (mg/g) is the amount of cobalt adsorbed per gram of the adsorbent at equilibrium,  $C_o$  (mg/L) is the initial concentration of cobalt,  $C_e$  (mg/L) is the concentration of cobalt at equilibrium,  $V$  (L) is the volume of solution and  $m$  (g) is the weight of red mud adsorbent.

### Equilibrium studies

The Langmuir and Freundlich isotherm models are the simplest and most commonly used isotherms to represent the adsorption of

components from a liquid phase onto a solid phase. In an adsorption isotherm study, several equilibrium models have been developed to describe adsorption isotherm relationships. The Langmuir and Freundlich models are the world-widely used models because of their simplicity (Langmuir, 1918; Freundlich, 1906; Seader and Henly, 2006; Jiang et al., 2008).

## RESULTS AND DISCUSSION

### Calibration curve

Linear regression is one of the most frequently used analyses in calibration. Once the relationship between the input value and the response value assumed to be represented by a straight line is established, the calibration curve is used in the evaluation of accuracy of the result. From the calibration curve in Figure 1, it was observed that there is an approximate linear relationship between absorbance and cobalt concentration in the aqueous solutions. It is observed that the regression coefficient ( $R^2$ ) is quite high, and its value is 0.9908.

### Effect of contact time

Figure 2 shows the effect of contact time on the removal of cobalt by red mud waste material. These data have been obtained at initial cobalt concentration, pH, red mud dose, agitation speed and temperature equal to 30 mg/ml, 5.0, 2 mg/L, 500 rpm and 30°C, respectively. It can be seen from Figure 2 that the adsorption is so fast at initial contact time. At the first 15 min of contact time, the concentration of cobalt ions in aqueous solution reaches 18.045 mg/g of their equilibrium concentration. This indicates that the minimum contact time necessary for a good heavy metal removal is 15 min. This indicates that the maximum cobalt removal is achieved within 15 min after which concentration of cobalt in the solution decreases. This may be explained by the fact that initially for adsorption, large number of vacant sites was available, which slowed down later due to exhaustion of the remaining surface sites and repulsive force between solute molecule and bulk phase (Benhammou et al., 2005; Altundogan et al., 2000). The rapid removal of the adsorbate has significant practical importance as it will facilitate smaller reactor volumes ensuring efficiency and economy (Wang et al., 2005; Kalkan, 2006).

### Effect of pH

The effect of pH on the removal of cobalt ions is as shown Figure 3. It can be seen from Figure 3 that the adsorption of metal ions increases significantly as pH increases and adsorption reaches its maximum at pH equal to 5.5. More increase in pH values leads to metal precipitation and metal accumulation on red mud surface

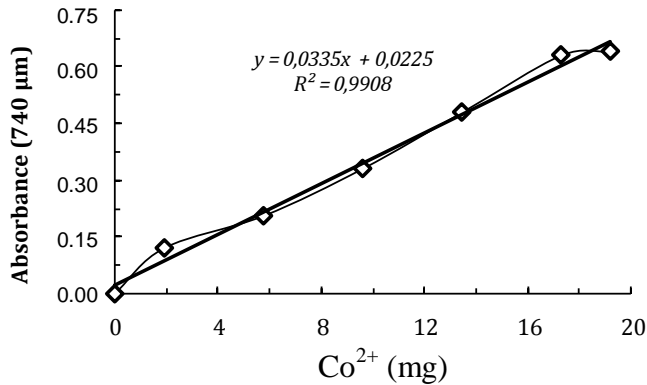


Figure 1. Calibration curve of cobalt adsorption.

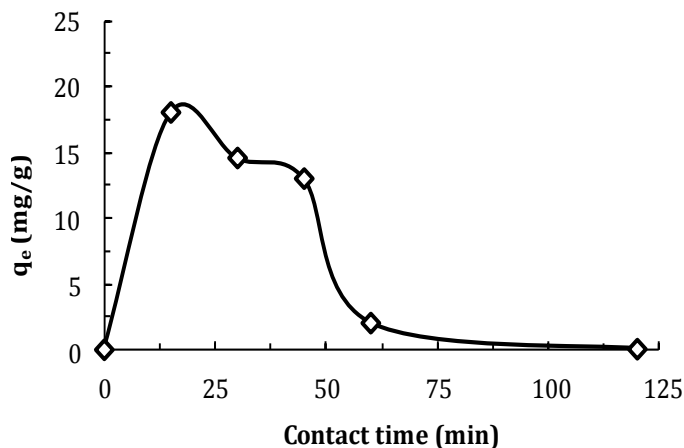


Figure 2. Removal of cobalt as a function of equilibrium time (pH: 5.5, initial cobalt concentration: 1 mg/ml, red mud dose: 1 g/30 ml, agitation speed: 500 rpm and temperature:  $30 \pm 1^\circ\text{C}$ ).

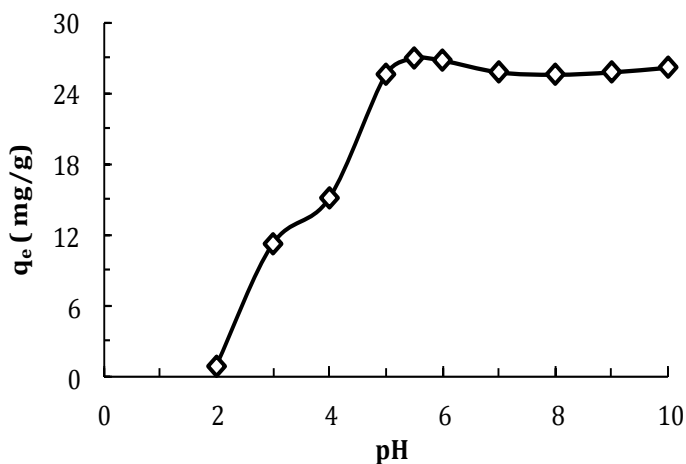


Figure 3. Effect of cobalt as a function of pH (initial arsenic concentration: 1 mg/ml, red mud dose: 1 mg/30 ml, agitation speed: 500 rpm and temperature:  $30 \pm 1^\circ\text{C}$ ).

deteriorated the adsorption mechanism (Ghassabzadeh et al., 2010).

From the results, it is evidence that maximum adsorption of cobalt at pH 5.5 of the solution play a very important role in the metal ions adsorption. This is partly because hydrogen ions themselves are strongly competing with metal ions (Sari et al., 2007). Surfaces possessing highly charged groups in aqueous solvents are especially sensitive to environmental conditions, such as pH. As the pH of the aqueous phase is lowered, a solid surface will usually become more positive or less negative (Alkan et al., 2005; Talip et al., 2009).

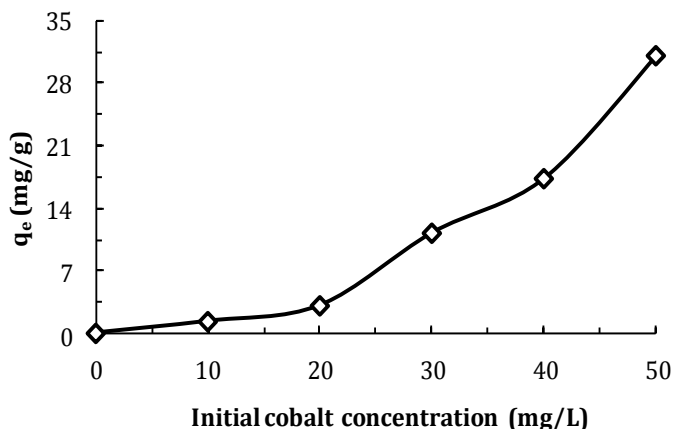
Red mud is a metal oxide adsorbent containing different metal oxides in the structure. Hydroxylated surfaces of these oxides developed charge on the surface of the water. It can be due to the interaction between cobalt ion and metal oxide. The removal of cobalt pollutant from aqueous solution by adsorption is highly dependent on the pH of the media which affects the surface charge of the solid particles and degree of ionization and speciation of adsorbate (Wang et al., 2005; Cengeloglu et al., 2006; Wang et al., 2008).

#### Effect of initial metal concentration

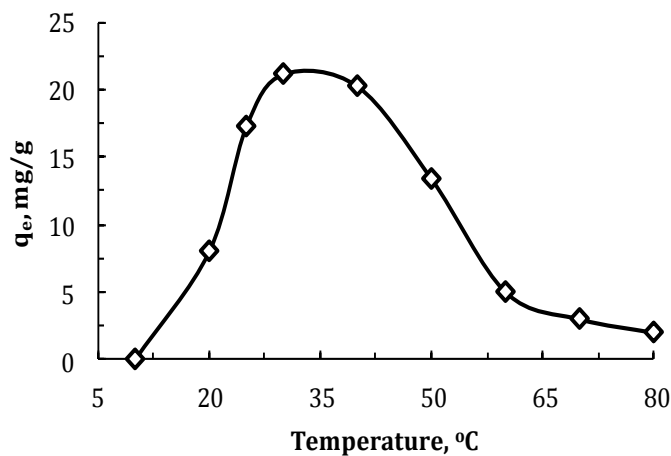
In order to establish the equilibration time for maximum uptake and to know the kinetics of the adsorption process, cobalt adsorption on red mud adsorbent was investigated as a function of initial cobalt concentration and the results are as shown in Figure 4. The initial concentration of cobalt provides the necessary driving force to overcome all mass-transfer resistance of metals between the aqueous and solid phases. Hence, a higher initial metal concentration will have a benefit effect on the red mud sorption capacity. From Figure 4, it seems that the equilibrium adsorption capacity increases essentially linearly with an increase in the initial metals concentration up to 50 mg/L for cobalt ion. Figure 4 shows that with increase in the initial concentration of cobalt from 2 to 50 mg/L, the amount adsorbed increases from 1.31 to 31.05 mg/g. At a higher initial concentration, the available sites of adsorption become fewer and hence the percentage adsorption depends on the initial concentration. For a fixed adsorbent dose, the total available adsorption sites are limited, thereby adsorbing almost the same amount of the adsorbate, thus resulting in a decrease in percentage adsorption corresponding to an increase in initial adsorbate concentration (Calisir et al., 2009).

#### Effect of temperature

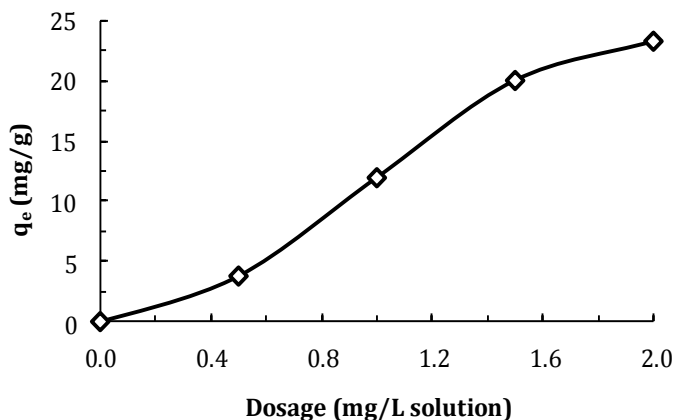
The effect of temperature influencing the adsorption has been studied in the range of 10 to 80°C and the effect of temperature on the adsorption of cobalt is as shown in Figure 5. It is observed that the degree of adsorption increases with increasing temperature and maximum



**Figure 4.** Effect of initial cobalt concentration on the adsorption of cobalt.



**Figure 5.** Effect of cobalt as a function of temperature (pH: 5.5, initial cobalt concentration: 1 mg/ml, red mud dose: 1 g/30 ml, agitation speed: 500 rpm).



**Figure 6.** Effect of red mud dosage on adsorption of cobalt (pH: 5.5, initial cobalt concentration: 1 mg/ml, red mud dose: 1 g/30 ml, agitation speed: 500 rpm).

adsorption of cobalt ions are obtained at 30°C, which is the temperature of the solution. An increase in temperature involves an increased mobility of the metal ions and a decrease in the retarding forces acting on the diffusing ions. Since adsorbent is porous in nature and the possibilities of diffusing the adsorbate cannot be ruled out, therefore, increase in the sorption with the rise of temperature may be diffusion controlled which is an endothermic process, that is, the rise of temperatures favors the adsorbate transport within the pores of adsorbent (El-Shafey, 2005).

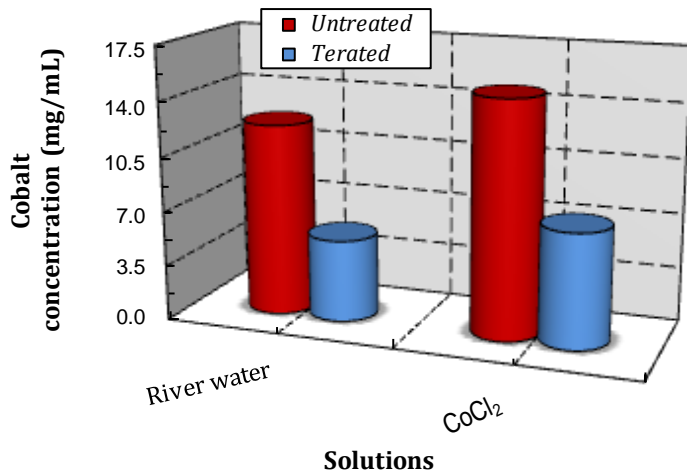
### Effect of adsorbent dosage

The effect of adsorbent dosage on the removal of cobalt ions is as shown Figure 6. These data have been obtained at an initial cobalt concentration, pH and temperature equal to 30 mg/ml, 5.5 and 30°C, respectively. It can be seen from Figure 6 that the total amount of metal ions removed from the solutions increases by the amount of adsorbent. The increase in the removal efficiency may be attributed to the fact that with an increase in the adsorbent dosage, more adsorbent surface will be available for the solute adsorbed (Gence et al., 2003; Ghassabzadeh et al., 2010).

The amount of metal ions adsorbed per unit mass of the adsorbent of cobalt reached its maximum value at 2.0 mg/L red mud adsorbent dosage. The phenomenon of increase in removal of cobalt with increase in adsorbent dosage may be explained as with increase in adsorbent dosage, more and more surface becomes available for metal ion to adsorb and this increases the rate of adsorption (Langmuir, 1918; Rio et al., 2002; Bansal et al., 2009).

The cobalt concentration in the aqueous solution taken from samples of polluted river water solution treated with red mud indicates that red mud enhanced adsorption capacity. Without the addition of the red mud, the leachate cobalt concentration is approximately 12.307 and 15.104 mg/ml for polluted river water and CoCl<sub>2</sub> solutions, respectively. The addition of red mud strongly inhibited the leaching of cobalt in both solutions. When the red mud is added to the aqueous solutions contaminated with cobalt, the concentration of cobalt in the leachate drastically reduces, whereas the adsorption capacity increases. The cobalt concentration in the samples of red mud treated leachates solutions decreases from 12.307 to 5.256 and from 15.104 to 7.307 for the polluted river water and CoCl<sub>2</sub> solutions, respectively. In each sample of red mud treated aqueous solution; it is seen that the adsorption in the cobalt ions is obtained using red mud adsorbent. The cobalt concentration in the red mud treated aqueous solutions was decreased using red mud as shown in the Figure 7.

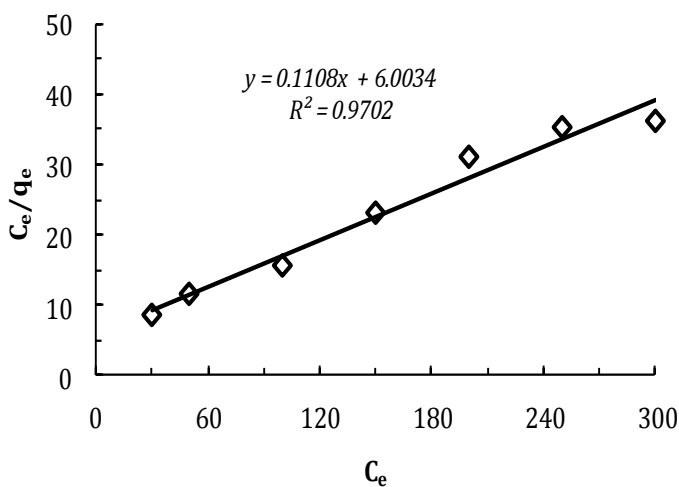
The increase in the adsorption capacity of red mud



**Figure 7.** Variation of cobalt concentration with red mud on the river water and CoCl<sub>2</sub>.

**Table 4.** Values of adsorption isotherm parameters for adsorption of cobalt.

Adsorption isotherm	Value
<b>Langmuir constant</b>	
<i>Q<sub>o</sub></i> (mg/g)	9.0252
<i>b</i> (L/mg)	0.0184
<i>R</i> <sup>2</sup>	0.9702
<b>Freundlich constant</b>	
<i>K<sub>F</sub></i> (mg/g)	0.0624
<i>n</i>	2.9481
<i>R</i> <sup>2</sup>	0.9335



**Figure 8.** Langmuir isotherm for the adsorption of cobalt.

treated aqueous solutions was attributed to the pH values and active components of red mud. The samples of polluted river water treated with red mud reached their

minimum point values in the cobalt concentration. The cancrinite and hematite minerals (Table 3) gave adsorbing capacity to the red mud and they, at the pH equilibrium in the adsorption experiments, had a negative charge density in its lattice. This should be neutralized by metal adsorbed with outer-sphere bonds on the external surfaces and by the incorporation of metals in the cages and channels of cancrinite framework if the hydrated ionic radius of the metals is compatible with the sizes of cancrinite cavities. Thus, the red mud, which contains higher quantities of this tectosilicate, adsorbed more cations (Whittington et al., 1998; Mon et al., 2005; Santona et al., 2006; Mahabadi et al., 2007). Because the pH of solutions at equilibrium in the experiments was lower than the point of zero charge of the red mud, the adsorption of heavy metals on the hydroxides occurred on positively charged surfaces through the formation of specific inner-sphere bonds. The hydroxides of the red mud, principally the hematite (Table 3), were the other active components in heavy metal adsorption (Apak et al., 1998; Lopez et al., 1998; Santona et al., 2006).

**Adsorption models**

The Langmuir and Freundlich isotherm models are the simplest and most commonly used isotherms to represent the adsorption of components from a liquid phase onto a solid phase. The adsorption data obtained from this study has been correlated with the Langmuir and Freundlich isotherm models.

**Langmuir model**

The Langmuir adsorption isotherm model represents one of the first theoretical treatments of non-linear sorption and suggests that the uptake occurs on a homogenous surface by monolayer sorption without interaction between the adsorbed molecules (Bansal et al., 2009). The linear form of the Langmuir adsorption isotherm is represented as:

$$C_e/q_e = [1/Q_o b + C_e/Q_o] \tag{2}$$

where *C<sub>e</sub>* (mg/L) is the equilibrium concentration of adsorbate in solution, *q<sub>e</sub>* (mg/g) is the amount of cobalt adsorbed per gram of the adsorbent at equilibrium, *Q<sub>o</sub>* (mg/g) is the Langmuir constants related to adsorption capacity and *b* (L/mg) is the equilibrium adsorption constant. *Q<sub>o</sub>* and *b* (Table 4) were calculated from the slope and intercept of the Langmuir plot of *C<sub>e</sub>* versus *C<sub>e</sub>/q<sub>e</sub>* (Figure 8).

**Freundlich model**

Freundlich adsorption isotherm model can be applied for

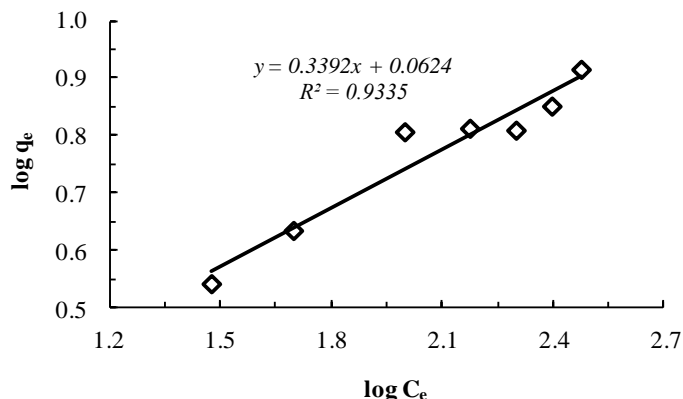


Figure 9. Freundlich isotherm for the adsorption of cobalt.

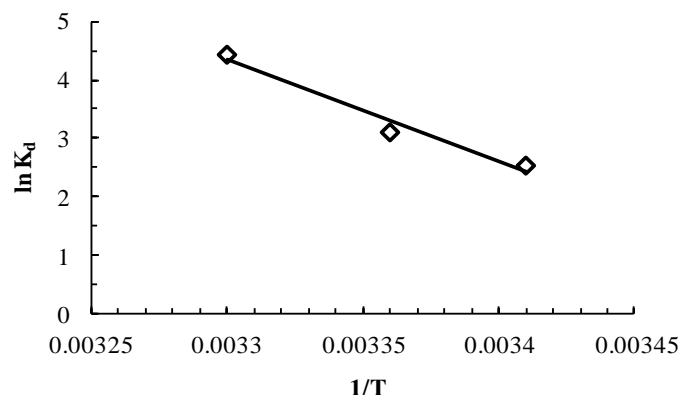


Figure 10. Influence of temperature on the thermodynamic behavior of adsorption of cobalt onto red mud adsorbent.

non-ideal sorption onto heterogeneous surfaces involving multilayer sorption. The linearized Freundlich isotherm model was applied for the adsorption of cobalt and is expressed as:

$$\log_{10} q_e = \log_{10} (K_F) + (1/n) \log_{10} (C_e) \quad (3)$$

where  $q_e$  (mg/g) is the amount of cobalt adsorbed per gram of the adsorbent at equilibrium,  $C_e$  (mg/L) is the equilibrium concentration of the adsorbate in solution,  $q_e$  (mg/g) is the amount of cobalt adsorbed per gram of the adsorbent at equilibrium.  $K_F$  and  $n$  are the constants incorporating all factors affecting the adsorption process (adsorption capacity and intensity) (Bansal et al., 2009).  $K_F$  and  $n$  values (Table 4) were calculated from the intercept and slope of the plot (Figure 9).

### Thermodynamic studies

The sorption capacity of red mud adsorbent increased with increase in the temperature of the system from 293

to 303 K. Thermodynamic parameters, such as change in free energy ( $\Delta G^\circ$ ) kJ/mol, enthalpy ( $\Delta H^\circ$ ) kJ/mol and entropy ( $\Delta S^\circ$ ) J/Kmol were determined using the following equations:

$$K_d = C_s / C_e \quad (4)$$

$$\Delta G^\circ = -RT \ln K_d \quad (5)$$

$$\ln K_d = (\Delta S^\circ / R) - (\Delta H^\circ / RT) \quad (6)$$

where  $K_d$  is the equilibrium constant,  $C_s$  is the solid phase concentration at equilibrium (mg/L),  $C_e$  is the liquid phase concentration at equilibrium (mg/L),  $T$  is the temperature in Kelvin, and  $R$  is the gas constant. From the temperature variation from 293 to 303 K on the sorption,  $\Delta H^\circ$  and  $\Delta S^\circ$  were obtained (Figure 10). The  $\Delta H_{ads}^\circ$  and  $\Delta S_{ads}^\circ$  values obtained from the slope and intercept of Van't Hoff plots are as shown in Table 5. Gibbs free energy ( $\Delta G$ ) was calculated as:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S - T\Delta S \quad (7)$$

The values of the thermodynamic parameters for the sorption of Co(II) on red mud adsorbent are as shown in Table 5.

The positive value of enthalpy change,  $\Delta H_{ads}^\circ$ , shows that the adsorption of cobalt is endothermic. The value of  $\Delta G_{ads}^\circ$  for these processes becomes less negative with increasing temperature, which shows that sorption is less favored at high temperatures as shown in Table 2, indicating that the reaction is spontaneous and more favorable at lower temperature. Adsorption heat values are acceptable at the chemisorption temperature levels.

Fixation of cobalt ions as a result of adsorption is attributed to a decrease in the degree of freedom of adsorbate ions, which gives rise to a negative entropy change (Rehman et al., 1995; Donat, 2010). The resultant effect of complex bonding and steric hindrance of the sorbed species eventually increases the enthalpy and entropy of the system.

### Conclusions

In this study, adsorption of cobalt on red mud has been investigated as a function of contact time, pH, initial metal concentration, temperature and adsorbent dose. The following conclusions have been drawn:

1. It has been shown that there is an approximate linear relationship between absorbance and cobalt concentration in the aqueous solutions. The regression coefficient is quite high, and its value is 0.9908.
2. The adsorption is so fast at initial contact time. At the first 15 min of contact time, the concentration of cobalt ions in aqueous solution reaches 18.045 mg/g of their equilibrium concentration.

**Table 5.** Thermodynamic parameters for the adsorption of cobalt onto red mud adsorbent.

$\Delta H_{\text{ads}}^{\circ}$ (kJmol <sup>-1</sup> )	$\Delta S_{\text{ads}}^{\circ}$ (kJmol <sup>-1</sup> )	$\Delta G_{\text{ads}}^{\circ}$ (kJmol <sup>-1</sup> )		
		293 K	298 K	303 K
0.145	51.44	-15.07	-15.33	-15.59

3. From the results, it is evidence that maximum adsorption of cobalt at pH 5.0 of solution play a very important role in the metal ions adsorption.

4. It can be seen that the equilibrium adsorption capacity seems to increase essentially linearly with an increase in the initial metals concentration up to 50 mg/L for cobalt ion.

5. The degree of adsorption increases with increasing temperature and maximum adsorption of cobalt ions are obtained at 30°C which is the temperature of the solution.

6. The cobalt concentration in the samples of red mud treated leachates solutions decreases from 12.307 to 5.256 and from 15.104 to 7.307 for the polluted river water and CoCl<sub>2</sub> solutions, respectively.

7. Based on the correlation coefficient values, it has been deduced that the Langmuir isotherm model better fitted to the experimental data. The high correlation coefficient showed that both adsorption isotherm models are suitable for describing the adsorption equilibrium of cobalt ions.

8. As shown in Table 5, the values  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  were positive for the adsorption of cobalt onto red mud. The positive value of  $\Delta H^{\circ}$  indicates that the adsorption process is endothermic in nature and the positive value  $\Delta S^{\circ}$  showed the increase in the degree of freedom or increase in the disorder of adsorption process.

9. The investigation shows that red mud is a very valuable material for the removal of cobalt ion from the aqueous solutions. The use of red mud for the removal of cobalt ion from aqueous solutions can potentially reduce the remediation costs.

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