

Chemical Modification of Zeolitic Tuff for Removal of Hg(II) from Water

Nida M. Salem, Rafat A. Ahmad and Akl M. Awwad
Industrial Chemistry Center, Royal Scientific Society,
P.O. Box 1438, Al-Jubaiha, 11941, Jordan

Abstract: The present study investigated the effectiveness of a Chemically Modified Jordanian Zeolitic Tuff (CMZT) as an adsorbent for the possible removal of toxic mercury from water. In this study, the effects of adsorbent dose, initial pH, initial concentration, contact time and temperature were examined. Thermodynamic analysis revealed that the adsorption behavior of Hg(II) onto the chemically modified Jordanian zeolitic tuff adsorbent was an endothermic process, resulting in higher adsorption capacities at higher temperatures. The negative values of ΔG° and positive values of ΔH° revealed that the adsorption process was spontaneous and endothermic. The Langmuir and Freundlich isotherm models were employed to fit the isothermal adsorption.

Key words: Hg(II), adsorption, water, chemically modified zeolitic tuff, isotherms, removal

INTRODUCTION

Mercury is one of the most toxic harmful metals in the environment because its toxicity and potential bioaccumulation. The maximum concentration of mercury recommended in drinking water is $2 \mu\text{g L}^{-1}$ by World Health Organization (WHO) and United States Environmental Protection Agency (EPA). Mercury released into the environment from chlor-alkali, paint, paper, oil refining, rubber processing paint, pulp, electrical and fertilizer industries. Various methods have been reported for the removal of mercury from water and waste waters such as precipitation, ion exchange, iron coagulation and electrodeposition. The adsorption technique is generally considered to be a promising method and has been studied for metals removal from water and wastewater. Recently, much research work has been done on the adsorption of mercury on various adsorbents such as laterite (Xiaohong *et al.*, 2008), clay minerals (Green-Ruiz, 2005), Fuller's earth (Oubagaranadin *et al.*, 2007) bentonites and modifying bentonites (Jin *et al.*, 1999; Li and Qian, 2006), natural and modified zeolitic minerals (Gebremedhin-Haile *et al.*, 2003), diatomite (Yuan *et al.*, 2005), soils (You and Luo, 1996), activated carbon (Zhang *et al.*, 2005; Zabihi *et al.*, 2010; Kadirvelu *et al.*, 2004) and agricultural wastes (Inbaraj and Sulochana, 2006); Feng *et al.*, 2004; Lohani *et al.*, 2008).

Zeolitic tuff is a general term for the consolidated pyroclastic rocks. These rocks can react with water and form zeolites by the transformation of the volcanic glass

which is the main original component of such rocks. Zeolitic tuffs are generally soft, friable and lightweight commonly contain 50-95% of one or more zeolite minerals that may coexist with unreacted volcanic glass and other mineral phases such as quartz, feldspar and calcite. Zeolites are hydrated aluminosilicates of alkaline and alkaline-earth metals that belong to the mineral class of tectosilicates. The structure of zeolites consists of a three-dimensional frame work of SiO_4 and AlO_4 tetrahedrons. The aluminum ion is small enough to occupy the position in the centre of the tetrahedron of four oxygen atoms and the Al^{3+} replacement for Si^{4+} raises a negative charge in the lattice. The net negative charge is balanced by an extra frame work cation, usually alkaline and alkaline earth elements.

MATERIALS AND METHODS

Preparation of chemically modified zeolitic tuff: Zeolitic Tuff (ZT) samples from Jabal Aritayn (30 km Azraq-Jordan), kindly supplied by Jordan factory for soil development and moisture drying CO. ZT was ground using a grinding mill (Retsch RM 100) to obtain particles of zeolitic tuff with dimensions between 0.08 and 2.5 mm and then sieved to obtain 0.5-2 mm sized fraction. The 0.5-2 mm sized fraction of ZT was washed with distilled water to remove soluble elements and other surface adhered particles and dried at 105°C . The chemical composition (wt %) of the zeolitic tuff sample utilized was $\text{SiO}_2 = 40.36$, $\text{Al}_2\text{O}_3 = 12.06$, $\text{Fe}_2\text{O}_3 = 11.64$, $\text{TiO}_2 = 2.85$, $\text{MgO} = 9.67$, $\text{CaO} = 9.77$, $\text{K}_2\text{O} = 1.43$, $\text{Na}_2\text{O} =$

1.85, P₂O₅ = 0.49 with loss of ignition = 8.85. Dried ZT was treated with concentrated hydrochloric acid (0.32 mass fraction purity) with agitation from time to time and left overnight. An aqueous colored acid solution which formed was separated from zeolitic tuff sample by decantation and filtration. The Chemically modified zeolitic tuff (CMZT) sample was washed with distilled water and dried at temperature 105°C and passed through 0.044 mm sieve to ensure the material uniformity. The specific surface areas of adsorbent were determined by N₂ adsorption at 77.4 K with a high-speed gas sorption analyzer (NOVA 4000, USA). It was found that surface area = 130.2 m²g⁻¹, pore width = 88.4 Å and pore volume = 6.5×10⁻² cm³ g⁻¹.

Preparation of Hg(II) stock solution: An Hg(II) stock solution 1000 mg L⁻¹ was prepared by dissolving 1.6195 g of mercury nitrate [Hg(NO₃)₂, Merck, Germany] in 1000 mL of double distilled water. A working solution for the experiments was freshly prepared from the stock solution. The working solutions with different concentrations of Hg(II) were prepared by appropriate dilutions of the stock solution immediately prior to their use. Standard acid 0.1 M HNO₃ and a base solution 0.1 M NaOH were used for pH adjustment. All of the reagents were of analytical grade and used without further purification.

Adsorption isotherm study: Adsorption equilibrium was obtained by shaking 1 g of dry adsorbent Phillipsite-magnesioferrite in a series of 100 mL flasks containing 20 mL of initial concentration of Hg(II) ions ranging from 10-40 mg L⁻¹ for 120 min. The initial pH value of Hg(II) solutions was adjusted from 1.0-11.0 with either 0.1 M HNO₃ or 0.1 M NaOH at 20, 30 and 40°C. Flasks were agitated on a shaker at 350 rpm constant shaking rate for 120 min to ensure equilibrium was reached and filtered through filter paper (Schleicher and SchUI 589) and the supernatant was analyzed for mercury by a sequential plasma emission spectrometer (ICPS-7510, Shimadizu). Each experiment was run in triplicate and mean values were reported.

The percentage mercury removal, R(%) was calculated for each run by Eq. 1:

$$R(\%) = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

where, C_i and C_e are the initial and the final concentrations of Hg(II) in the solution in mg L⁻¹.

The adsorption capacity of the adsorbent for each concentration of Hg(II) at equilibrium was calculated using Eq. 2:

$$q_e (\text{mg g}^{-1}) = \frac{C_i - C_e}{M} \times V \quad (2)$$

Where:

C_i = The initial concentration of Hg(II)

C_e = The final concentration of Hg(II)

V = The volume of the solution (L)

M = The mass of adsorbent (g) used

RESULTS AND DISCUSSION

Characterization of chemically modified zeolitic tuff

adsorbent: The XRD analysis indicated that the examined CMZT minerals derived from zeolitic tuff sample is rich in phillipsite-K mineral, [(K₂)_{0.48} Ca_{0.52} Al₂Si₄O₁₂.xH₂O], amorphous silica and with some magnesioferrite [Mg Fe₂O₄]. The method used in this work for chemical modification of ZT allows the separation of approximately 100 w (mass fraction) = 25-30 of other volcanic constituents (iron, aluminium, magnesium, calcium and sodium oxides). FTIR absorption bands of Zeolitic Tuff (ZT) and Chemically Modified Zeolitic Tuff (CMZT) are showed in Fig. 1 which indicated that the band of ν CO₃ at 1426 cm⁻¹ in ZT disappeared in CMZT and the band of ν Si-O-Al at 1022 cm⁻¹ was shifted to 1049 cm⁻¹ which appears as a strong and broad band due mainly to phillipsite-K indicating that it is the major constituent of CMZT. XRF analysis showed that the chemically modified zeolitic tuff is rich in SiO₂, Al₂O₃ with a percent oxide composition 51.92 and 10.02, respectively. The moderate high SiO₂/Al₂O₃ ratio of 5.18 gives rise to good selectivity (Erdem *et al.*, 2002).

Effect of the initial pH: The effect of pH of the Hg(II) solution on adsorption capacity of Hg(II) onto the CMZT is shown in Fig. 2. It can be shown from Fig. 2 that the removal Hg(II) percent increases sharply with increasing pH of Hg(II) from (1.0-9.0) and then decreases to reach pH 11.0. The adsorption capacity of CMZT is low at low pH because large quantities of protons compete with mercury cations for the adsorption sites. As the pH of the solution increases, the number of protons dissociated from functional groups on the surface of CMZT increases and thus more negative groups for complexation of mercury cations are provided.

Effect of adsorbent dose: It was observed that the percentage removal of Hg(II) increases with the increase in adsorbent dosage but beyond a certain value 1.5-2.0 g, the percentage removal reaches almost a constant value. The increase in efficiency of Hg(II) removal may be attributed to the fact that with an increase in the adsorbent dose more adsorbent surface or more adsorption sites were available for the mercury ions to be adsorbed. A maximum removal of 98.89% was observed at adsorbent dosage of 1 g L⁻¹ at pH 9.0 for an initial Hg(II) concentration of 40 mg L⁻¹ and at temperature 40°C.

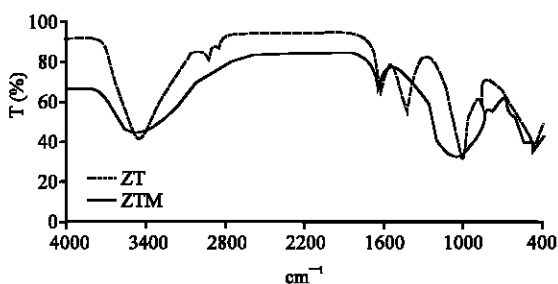


Fig. 1: FTIR spectra of raw Zeolitic Tuff (ZT) and Chemically Modified Zeolitic Tuff (CMZT)

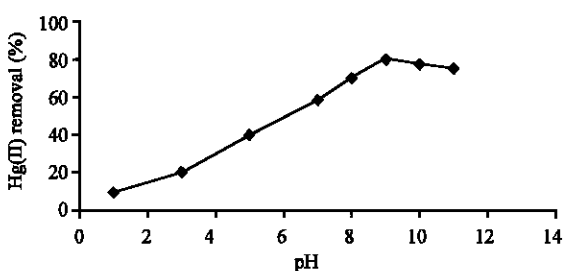


Fig. 2: Effect of pH on Hg(II) adsorption by CMZT at 30°C and an initial concentration of 40 mg L⁻¹

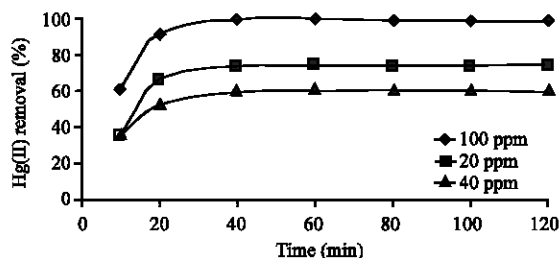


Fig. 3: Effect of contact time and initial Hg(II) concentration on Hg(II) adsorption by CMZT at 40°C and pH 9.0

Effect of contact time and initial Hg(II) concentration:

The effect of contact time and initial concentration of Hg(II) on adsorption of Hg(II) onto CMZT is shown in Fig. 3. It can be seen from Fig. 3 that the removal percent of Hg(II) increases with contact time and initial concentration until equilibrium is attained between the amount of Hg(II) on CMZT and the remaining Hg(II) in solution. Figure 3 shows that the removal percent of Hg(II) increases with contact time from 0-60 min and then becomes almost constant up to the end of the experiment. It can be concluded that the binding of Hg(II) with CMZT is high at initial stages and becomes almost constant after an optimum contact time of 60 min. The Hg(II) removal

percent versus time curves are smooth and continuous leading to saturation, suggesting possible monolayer coverage of Hg(II) ions on the surface of the CMZT.

Effect of temperature and thermodynamic parameters:

As temperature increased from 20-40°C, Hg(II) removal percent increased from 70.04-98.89% for an initial concentration of 40 mg L⁻¹ at pH 9.0. Similar trends were observed for other concentrations. This indicated that the adsorption process is endothermic in nature. In the present research, the thermodynamic behavior of the adsorption of Hg(II) ions onto CMZT is evaluated as follows. The changes in Gibbs energy, ΔG°, of the adsorption process is related to the equilibrium constant by the Eq. 3:

$$\Delta G^\circ = -RT \ln K_c \tag{3}$$

where, K_c is the equilibrium constant calculated from the Eq. 4:

$$K_c = \frac{C_{Ae}}{C_e} \tag{4}$$

where, C_{Ae} and C_e are the equilibrium concentration of Hg(II) (mg L⁻¹) on CMZT adsorbent and in solution, respectively. The obtained values of K_c at different temperatures are shown in Table 1.

The enthalpy change, ΔH° and entropy change, ΔS° were obtained from the van't Hoff (Eq. 5):

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{5}$$

Where:

T = The absolute temperature (K)

R = The gas constant (8.314 Jmol⁻¹ K⁻¹)

ΔH° (kJmol⁻¹) and ΔS° (Jmol⁻¹ K⁻¹) were calculated from the slope and intercept of a linear plot of ln K_c versus 1/T. The plot shown in Fig. 4 is linear over the entire range of temperatures investigated.

The thermodynamic parameters were evaluated at three operating temperatures, 20, 30 and 40°C, at an initial Hg(II) concentration of 20 mg L⁻¹. The values of K_c, ΔH°, ΔS° and ΔG° at the investigated temperatures are shown in Table 1. The obtained negative values of ΔG° at all temperatures studied revealed the fact that the adsorption process was spontaneous. Positive values of ΔH° indicate the endothermic nature of the adsorption process. The positive value of ΔS° suggests increased randomness of the solid/solution interface during the adsorption of Hg(II) ions onto CMZT adsorbent.

Table 1: Equilibrium constant, K_c and thermodynamic parameters

T(°C)	K_c	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (JK ⁻¹ mol ⁻¹)
20	3.425	-2.999	24.607	94.339
30	4.995	-4.052	-	-
40	6.553	-4.896	-	-

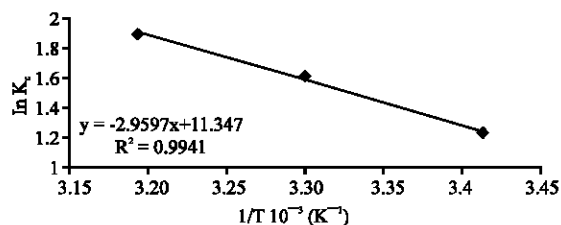


Fig. 4: $\ln K_c$ versus $1/T$

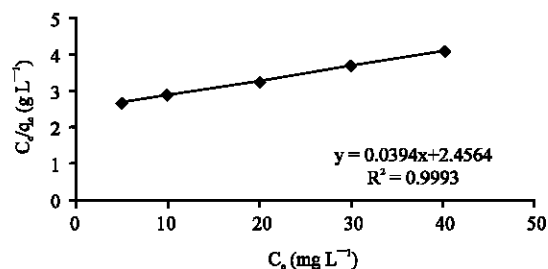


Fig. 5: Langmuir plot for Hg(II) adsorption on CMZT

Adsorption isotherms: Adsorption data for a wide range of adsorbate concentration are most conveniently described by adsorption isotherms. The experimental data for the removal of Hg(II) by CMZT were processed using the Langmuir and Freundlich isotherm models. The data were found to fit both models.

The Langmuir isotherm model is given by the following Eq. 6:

$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{1}{Q_m} C_e \quad (6)$$

Where:

- q_e = The milligrams of arsenic adsorbed per gram of the adsorbent
- C_e = The mercury concentration in the final solutions (mg L⁻¹)

Q_m (mg g⁻¹) and b (L g⁻¹) are Langmuir constants related to sorption capacity and sorption energy, respectively. Maximum adsorption capacity denoted by Q_m represents monolayer coverage of Hg(II) with adsorbent and b implies the enthalpy of adsorption which should vary with temperature. A linear plot (Fig. 5) is obtained by plotting C_e/q_e against C_e over the entire range of mercury concentration investigated.

Table 2: Parameters of langmuir and freundlich isotherm for the adsorption of Hg(II) on CMZT

Models	Values
Langmuir	
Q_m (mgg ⁻¹)	25.3810
b (mgL ⁻¹)	0.0015
R^2	0.9990
Freundlich	
K (mg g ⁻¹)	0.5350
$1/n$ (L g ⁻¹)	0.8030
R^2	0.9960

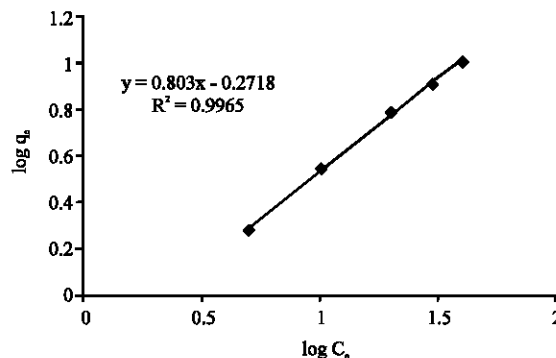


Fig. 6: Freundlich plot for Hg(II) adsorption on CMZT

Langmuir parameters Q_m and b , together with the regression coefficients R^2 determined from the plot shown in Table 2 confirm a good agreement between the theoretical model and experimental results obtained. Q_m values are computed from slope while b values from the intercept. Langmuir Q_m and b values increased with temperature, showing that the adsorption capacity and intensity of adsorption are enhanced at higher temperatures.

The Freundlich isotherm model could be applied to the sorption process which describes the physical adsorption of Hg(II) only. In contrast to the Langmuir monolayer model, the Freundlich isotherm is a consecutive layer model which does not predict any saturation of the adsorbent by Hg(II). The linearized form of the Freundlich isotherm used to evaluate the different sorption parameters is:

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (7)$$

Where:

- C_e = The equilibrium concentration (mg L⁻¹)
- q_e = The amount adsorbed at equilibrium (mg g⁻¹)

K and n are the isotherm constants are calculated from the intercepts and slopes of the Freundlich plots of $\log q_e$ against $\log C_e$ (Fig. 6). Freundlich parameters, K and n together with the regression coefficients R^2 determined from the plot are shown in Table 2 and confirmed a good agreement between the theoretical model and experimental results obtained.

CONCLUSION

The results in this study demonstrate that Chemically Modified Zeolitic TUFF (CMZT) is an effective adsorbent and can be successfully used as an adsorbing agent for the removal of Hg(II) ions from water. pH is a principal factor affecting the adsorption of Hg(II) onto CMZT. The alkaline environment (pH 8-10) is favorable to the adsorption of Hg(II) on CMZT. Lower pH values are unfavorable to the adsorption of Hg(II). The thermodynamic parameters, ΔH° , ΔS° and ΔG° values of Hg(II) adsorption onto show endothermic heat of adsorption, favored at higher temperatures. The positive value of ΔS° revealed an increase in randomness of the solid/solution interface during the adsorption of Hg(II) ions. Regression coefficients R^2 were found to be >0.999 and 0.996 revealing the best fit for the adsorption data by the Langmuir and the Freundlich isotherm models.

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