

## A study on removal characteristics of copper from aqueous solution by sewage sludge and pomace ashes

J. Bouzid<sup>a,\*</sup>, Z. Elouear<sup>a</sup>, M. Ksibi<sup>a</sup>, M. Feki<sup>b</sup>, A. Montiel<sup>c</sup>

<sup>a</sup> *Laboratoire Eau Energie et Environnement, Ecole Nationale d'Ingénieurs de Sfax, BP W 3038 Sfax, Tunisia*

<sup>b</sup> *Unité de Chimie Industrielle et Matériaux, Ecole Nationale d'Ingénieurs de Sfax, BP W 3038 Sfax, Tunisia*

<sup>c</sup> *Société Anonyme de Gestion des Eaux de Paris, 9 rue Schoelcher, 75675 Paris Cedex 14, France*

Received 25 April 2007; received in revised form 17 July 2007; accepted 18 July 2007

Available online 2 August 2007

### Abstract

In the present work, the abilities of sewage sludge and pomace ashes to remove copper ( $\text{Cu}^{2+}$ ) ions from aqueous solutions are compared. Batch adsorption experiments were performed in order to evaluate the removal efficiency of these materials. Effect of contact time, solution pH, ash concentration and temperature on the removal of  $\text{Cu}^{2+}$  was investigated. The results of batch equilibrium studies showed that the solution pH was the key factor affecting the adsorption characteristics. In general, the amount of Cu removed increased as the solid concentration and pH increased, and then it remained constant over a wide pH region. The adsorption test of applying sewage sludge and pomace ashes into synthetic wastewater revealed that the adsorption data of these materials for copper ions were better fitted to the Langmuir isotherm since the correlation coefficients for the Langmuir isotherm were higher than that for the Freundlich isotherm. The estimated maximum capacities of copper adsorbed by sewage sludge and pomace ashes were 5.71 and 6.98  $\text{mg g}^{-1}$ , respectively. Experimental results indicated that the adsorption was favorable at higher pH and higher temperature. Values of  $\Delta G^\circ$  ranging from  $-4.64$  to  $-5.13$   $\text{kcal mol}^{-1}$  for sewage sludge ash and from  $-4.97$  to  $-5.53$   $\text{kcal mol}^{-1}$  for pomace ash suggest that the adsorption reaction is a physical process enhanced by the electrostatic effect. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  are, respectively, 4.27  $\text{kcal mol}^{-1}$  and 30.6  $\text{cal K}^{-1} \text{mol}^{-1}$  for sewage sludge ash and 4.33  $\text{kcal mol}^{-1}$  and 31.3  $\text{cal K}^{-1} \text{mol}^{-1}$  for pomace ash. The mechanisms of copper removal by these materials included adsorption and precipitation. The sewage sludge and pomace ashes are shown to be effective adsorbents for this metal.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Adsorption; Copper ion; Pomace ash; Sewage sludge ash; Precipitation

### 1. Introduction

The potential sources of copper in industrial waste streams include metal cleaning and plating baths, pulp, paper and paper-board mills, wood pulp production, fertilizer industry, etc. [1]. Excessive intake of copper results in its accumulation in the liver. The chronic copper poisoning is related to hemochromatosis when present in large amounts [2]. It is also toxic to fish life even when its content is in low amounts in natural waters [2]. Removal of heavy metals from contaminated aquatic systems is deemed important for the protection of environmental health. Many technologies have been developed to remove heavy metals from contaminated waters, such as chemical precipitation,

ion exchange, membrane separation, biological treatment, and adsorption.

In the last few years, adsorption has been shown to be an alternative method for removing trace metals from water and wastewater. Although, the adsorbents commonly recommended for removal of heavy metals are alumina, silica, iron oxide and activated carbon [3,4]. The high cost of activated carbon and oxides has inspired the investigators to search for suitable and low-cost adsorbents. Among these, the use of fly ash has received particular attention as an economical adsorbent for removing heavy metals from wastewater due to the ash's content of alumina ( $\text{Al}_2\text{O}_3$ ), silica ( $\text{SiO}_2$ ), ferric oxide ( $\text{Fe}_2\text{O}_3$ ) and calcium oxide ( $\text{CaO}$ ). Fly ash is solid residue from incineration which is found in abundance in the world. Fly ash with high content of  $\text{CaO}$  or  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  is considered as strong alkali material and presents high pH in water. A number of studies were conducted to show the effectiveness of fly ash in the removal of

\* Corresponding author. Tel.: +216 20 413 488; fax: +216 74 665 190.

E-mail address: [Jalel.Bouzid@tunet.tn](mailto:Jalel.Bouzid@tunet.tn) (J. Bouzid).

Table 1  
Chemical composition of sewage sludge and pomace ashes

Samples	Composition													
	(%)										mg kg <sup>-1</sup>			
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	MgO	Na <sub>2</sub> O	As	Cu	Ni	Pb	Zn
Sewage sludge ash	19.95	9.02	20.98	2.07	9.00	16.6	23.05	2.47	0.92	– <sup>a</sup>	0.28	– <sup>a</sup>	0.146	1.23
Pomace ash	24.43	9.04	22.84	2.51	4.55	16.17	3.40	2.62	2.67	– <sup>a</sup>	– <sup>a</sup>	– <sup>a</sup>	– <sup>a</sup>	– <sup>a</sup>

<sup>a</sup> Not detected.

heavy metals ions, organic compounds especially phenolic compounds, dyes and other organic matters in waters [5–8]. The purpose of this study is to compare two different ashes (sewage sludge ash and pomace ash) corresponding to two abundant and wastes without any commercial value. However, they displayed both adsorbing and neutralizing capacities. They were for their ability to remove Cu<sup>2+</sup> from an aqueous solution and to assess the influence of different parameters such as contact time, solution pH, ash concentration and temperature on copper adsorption by these materials. The adsorption isotherms and mechanisms of removal of copper ions by these materials are evaluated.

## 2. Experimental

### 2.1. Materials and equipment

The sewage sludge sample used in this study was collected from Municipal Community Waste Water Treatment Plant in the south of Tunisia (Sfax city). Pomace, the waste material of olive oil industry, was obtained from olive oil factory in Sfax (Tunisia). The sampled dewatered sludge cake and pomace were first burned in a modular incinerator at 600 °C for 2 h to provide incineration ashes and then finely ground by a ball mill. The ground of sewage sludge and pomace ashes samples was further screened by 100 μm sieve. The finer part of these ashes passing through the 100 μm sieve was collected, tested, and used in the following experiments. The average diameter of the used adsorbents particules was around 60 μm.

Scanning electron microscope (SEM) (Philips XL30) and energy dispersive X-ray analysis (EDAX) (Philips ED AX 9100) were used to characterize the ashes samples for constituent and morphology. The surface area of ashes samples was determined by a BET-N<sub>2</sub> surface area analyzer (Model QS-7, Quantachrome Co., Greenvale, NY).

The pH of zero point of charge (pH<sub>zpc</sub>) was determined by adding a known amount of adsorbent (0.1 g) to a series of bottles that contained 50 mL of deionised water. Before adding the adsorbent, the pH of the solutions was adjusted to be in the range of 1.0–9.0 by the addition of either 0.1 M HNO<sub>3</sub> or 0.1 M NaOH. These bottles were then rotated for 1 h in a shaker and pH values were measured at the end of the test. The pH of the suspensions is represented as a function of the initial pH of the solutions. The curve obtained theoretically cross the bisector of axes at the point of zero charge. X-ray diffraction (XRD) patterns of all ashes samples were obtained with a Philips X'Pert

diffractometer using Cu Kλ radiation at 35 kV and 150 mA over the range (2θ) of 0–60°. Aqueous solutions containing copper ions (Cu<sup>2+</sup>) at various concentrations were prepared from copper salts (CuSO<sub>4</sub>·5H<sub>2</sub>O). All chemicals used for the treatment of the different sorbents and for adsorption tests were of analytical quality. The various solutions are prepared in distilled water.

A pH meter (models pH 540 GLP) equipped with a combined glass electrode SENTIX 41 was used to measure the pH of the solutions. A preliminary calibration is systematically carried out using suitable buffer solutions. The concentrations of copper ions were measured by an atomic absorption spectrometer (HITACHI Z-6100) by electrothermal atomization mode.

### 2.2. Batch experiments

Batch experiments included: the kinetic studies, pH effect and adsorption isotherms. Adsorption experiments for the kinetic study were conducted as follow: a series of bottles containing 1–30 g L<sup>-1</sup> ashes slurries and copper of concentration 500 mg L<sup>-1</sup> were kept in a shaker at room temperature. After shaking for different time intervals, the samples were collected and analyzed for residual concentrations. Batch adsorption experiments for the effect of initial pH on the adsorption process were conducted by preparing a series of 100 mL solutions containing various amounts of ashes (1–10 g L<sup>-1</sup>) and a fixed Cu(II) concentration of 500 mg L<sup>-1</sup> in 200 mL polyethylene bottles at different pH's. After initial pH adjustment in the range of 1–10 with HNO<sub>3</sub> or NaOH, the samples were incubated on a shaker for 1 h at room temperature. At the end of the mixing, the pH was measured. The ashes particles were separated from suspensions by filtration through a 0.45 μm membrane filter. For each individual adsorption experiment, with a designed copper concentration, a set of blank without ashes in the solutions was conducted to check the background of copper hydroxide precipitates. This background can serve as a reference level to assure that the total metal removal is not wrongly accounted owing to metal hydroxide precipitate itself. Adsorption isotherm studies were conducted by adding 0.1 g of ashes to a 100 mL solution containing various copper ion concentrations (10, 30, 50, 70, 100 mg L<sup>-1</sup>). The initial pH was maintained at 3 and the suspensions were stirred for 1 h. After filtration through a 0.45 μm membrane filter (MFS), the filtrates were analyzed. In order to determine the effect of temperature on adsorption phenomenon, isotherms were established at 10, 23 and 40 °C.

### 3. Results and discussion

#### 3.1. Physicochemical characterizations of ashes

As determined by EDAX, the predominant chemical compositions of sewage sludge and pomace ashes are given in Table 1. These results showed that the predominant chemical compositions of these ashes samples include silicon oxide, aluminum oxide, calcite and other oxides are present in trace amounts. It is thus expected that Cu(II) will be mostly adsorbed either by silica, alumina or by a combined influence of these oxides. In addition, the copper content in sewage sludge is  $0.28 \text{ mg kg}^{-1}$ . This value is lower than those reported ( $3.0\text{--}19.3 \text{ g kg}^{-1}$ ) by Tay and Show [9], Tay and Yip [10] and Tay et al. [11]. For this reason, the effect of copper ion, released from sewage sludge into solutions, can be ignored in the following experiments.

X-ray diffraction analysis results of sewage sludge and pomace before and after heating for 2 h at  $600^\circ\text{C}$  are presented in Fig. 1a and b, respectively. It can be seen that an increase in temperature definitely increases the level of mineralization since more peaks appear. In the case of materials obtained at  $600^\circ\text{C}$ , the degree of mineralization is much lower. The samples of sewage sludge and pomace dried at  $105^\circ\text{C}$  are predominantly amorphous. Combustion at  $600^\circ\text{C}$  results in formation of aluminosilicates, calcite and the oxides of aluminum, iron, magnesium, sodium and potassium [12].

The BET surface areas of sewage sludge and pomace ashes are found to be  $50.85$  and  $146.4 \text{ m}^2 \text{ g}^{-1}$ , respectively. These

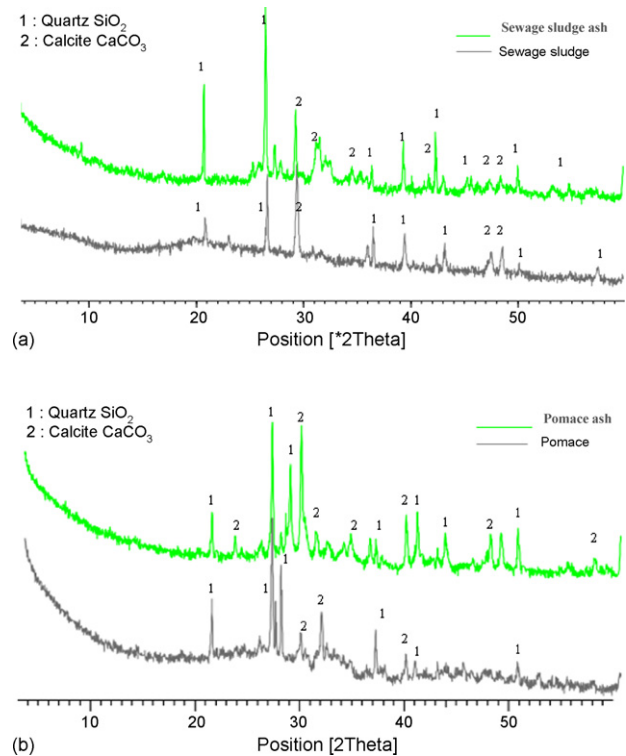


Fig. 1. X-ray diffraction patterns of (a) sewage sludge and (b) pomace before and after combustion at  $600^\circ\text{C}$ .

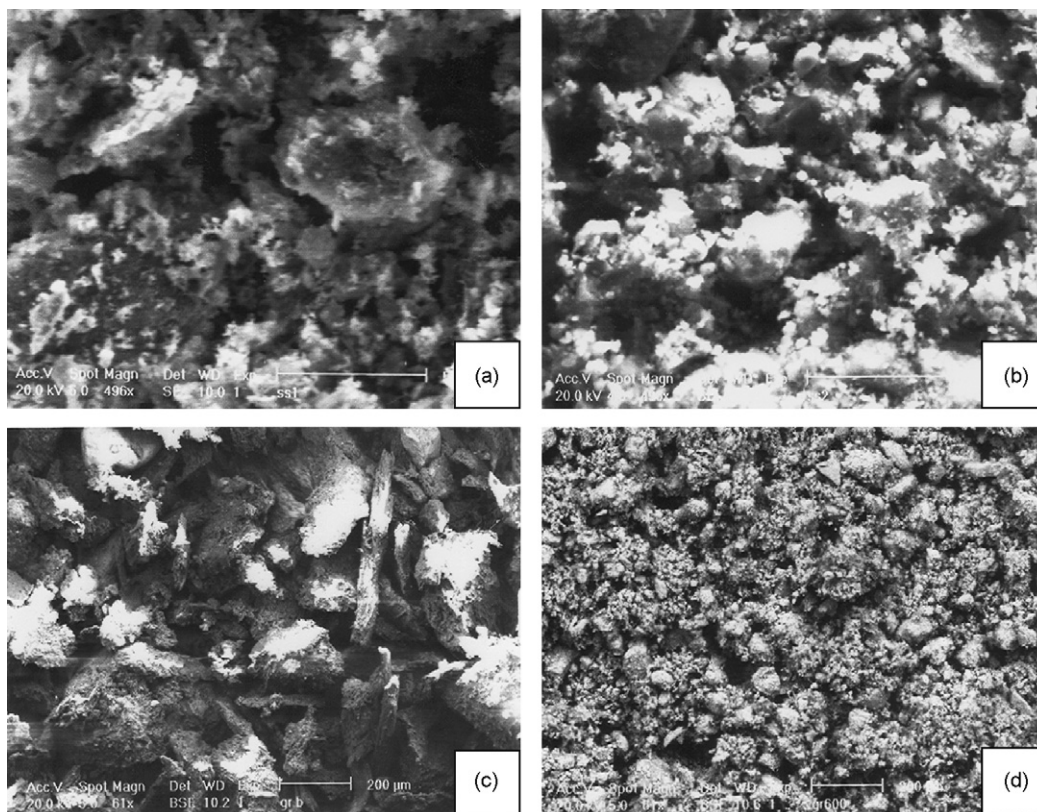


Fig. 2. Scanning electron micrograph of (a) sewage sludge; (b) sewage sludge ash; (c) pomace; (d) pomace ash.

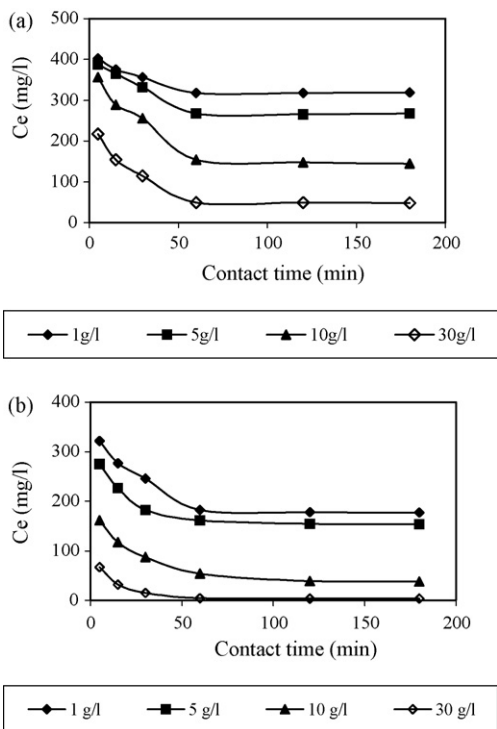


Fig. 3. Kinetic study for copper ion adsorption on (a) sewage sludge ash and (b) pomace ash. Experimental condition: initial Cu(II) = 500 mg/L, T: 23 °C and ash concentrations (1–30 g/L).

results revealed that the sewage sludge and pomace ashes are porous materials with significant pore surface area.

Fig. 2a–d shows SEM images of the sewage sludge and pomace before and after combustion at 600 °C. It can be seen that the surface morphologies of the raw and calcined samples are obviously different. SEM observation of samples heated at 600 °C (Fig. 2b and d) indicates the common feature of porous and irregular morphology of these ashes resulting in a large  $S_{BET}$ .

### 3.2. Effect of contact time

The time-course of adsorptive removal of Cu(II) and their uptake by sewage sludge and pomace ashes is shown in Fig. 3a and b, respectively. The rate of Cu(II) removal is found to be very rapid during the initial 30 min, and thereafter, it decreases considerably. No significant change in copper ion removal is observed after about 60 min. Hence, further experiments were carried out by fixing a contact time of 60 min for Cu<sup>2+</sup> sorption on sewage sludge and pomace ashes.

### 3.3. Equilibrium adsorption isotherms

Langmuir adsorption isotherm can be successfully applied to model the equilibrium adsorption data in a metal–surface system. The general form of the Langmuir equation is:

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (1)$$

where  $C_e$  is the equilibrium concentration of adsorbate ( $\text{mg L}^{-1}$ ),  $q_e$  the amount adsorbed at equilibrium ( $\text{mg g}^{-1}$

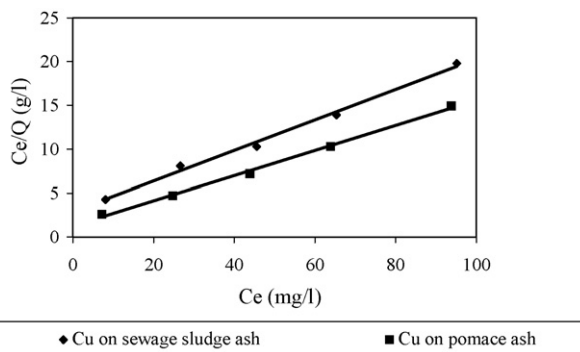


Fig. 4. The linear fitting of the Langmuir isotherms for Cu<sup>2+</sup> adsorption on sewage sludge ash and pomace ash at 23 °C and pH 3.

adsorbent), and  $Q$  ( $\text{mg g}^{-1}$ ) and  $b$  ( $\text{L mg}^{-1}$ ) are the Langmuir constants related to the adsorption capacity and energy, respectively. When  $C_e/q_e$  is plotted against  $C_e$ , a straight line with slope  $1/Q$  and intercept  $1/Qb$  is obtained (Fig. 4), which shows that the adsorption of copper follow Langmuir isotherm model. The Langmuir parameters,  $Q$  and  $b$ , are calculated from the slope and intercept of the graphs and are given in Table 2.

The experimental data was well correlated ( $R^2 > 0.99$ ) to the Langmuir equation. The fitted results indicate that the magnitude of  $Q$  is closely related to the kind of adsorbent. The adsorption affinity constants,  $b$ , are, respectively, for sewage sludge and pomace ashes equal to  $0.06 \text{ L mg}^{-1}$  and  $0.11 \text{ L mg}^{-1}$ .

The results of copper ion sorption onto sewage sludge and pomace ashes were also analyzed by using the Freundlich model to evaluate parameters associated to the sorption behaviour. The Freundlich equation has been widely used and is applicable for isothermal adsorption. The Freundlich equation has the general form:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (2)$$

where  $q_e$  is the amount of metal ions adsorbed per unit weight ( $\text{mg g}^{-1}$  adsorbent),  $C_e$  the equilibrium concentration ( $\text{mg L}^{-1}$ ) of adsorbate, and  $K_f$  and  $n$  are the Freundlich constant. When  $\log q_e$  is plotted against  $\log C_e$ , a straight line with slope  $1/n$  and intercept  $\log K_f$  is obtained. The intercept of line,  $\log K_f$ , is roughly an indicator of the adsorption capacity and the slope,  $1/n$ , is an indicator of adsorption intensity. The Freundlich parameters for the adsorption of copper ions are also given in Table 2. The fit to the linear form of the models was examined by calculation of the linearity coefficient ( $R^2$ ). Regression values ( $R^2$ ) presented in the Table 2, indicate that the adsorption data for Cu(II) removal fitted well the Langmuir model than the Fre-

Table 2  
Freundlich and Langmuir constants for Cu(II) adsorption on sewage sludge ash and pomace ash at 23 °C

	Langmuir model			Freundlich model		
	$Q$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{L mg}^{-1}$ )	$R^2$	$K_f$	$1/n$	$R^2$
Cu <sup>2+</sup> on sewage sludge ash	5.71	0.06	0.99	0.86	0.39	0.97
Cu <sup>2+</sup> on pomace ash	6.98	0.11	0.99	1.6	0.32	0.98

Table 3  
Adsorption capacity of Cu(II) by various adsorbents

Adsorbent	pH	Surface area ( $\text{m}^2 \text{g}^{-1}$ )	$Q$ ( $\text{mg g}^{-1}$ )	Source
Sewage sludge ash	3	50.85	5.71	This study
Pomace ash	3	146.4	6.98	This study
Fly ash	5	5.77	1.2	Panday et al. [13]
Fly ash (I)	5	0.34	0.34–1.35	Bayat [14]
Fly ash (II)	5	0.11	0.09–1.25	Bayat [14]
Bagasse fly ash	4	–	2.26–2.36	Gupta et al. [15]
Fly ash	5	1.15	1.7–8.1	Ayala et al. [16]
Olive stone waste	5.5	0.18	2.02	Fiol et al. [17]
Powdered waste sludge	–	–	27.7	Kargi et al. [18]
An electrochemically oxidized activated carbon cloth (EOACC)	5	532	101.6	Harry et al. [19]
Activated carbon (Ceiba pentandra hulls)	6	521	20.38	Madhava et al. [20]

undlich model ( $R^2 = 0.99$  and  $0.98$ , respectively) for all ashes. Consequently, the sorption of copper ions on sewage sludge and pomace ashes follows the Langmuir isotherm model where the uptake occurs on homogeneous surface by monolayer sorption without interaction between sorbed molecules.

A comparison of Cu(II) adsorption capacities onto various adsorbents was calculated using the Langmuir isotherm (Table 3). The Cu(II) adsorption capacity of sewage sludge ash is equal to  $5.71 \text{ mg g}^{-1}$  while this for pomace ash is equal to  $6.98 \text{ mg g}^{-1}$ . These values were significantly higher than fly ash [13–16] and lower than that of powder activated carbon ( $101.6 \text{ mg g}^{-1}$ ) [19]. Intuitively, this may be attributed in part to the small specific surface area ( $50.85 \text{ m}^2 \text{ g}^{-1}$ ) of sewage sludge ash and ( $146.4 \text{ m}^2 \text{ g}^{-1}$ ) of pomace ash compared to that of commercial activated carbon (e.g.  $532 \text{ m}^2 \text{ g}^{-1}$  for powder). Other parameters such as pH and temperature have influences on the adsorption process to various degrees.

### 3.4. Effect of pH on Cu(II) adsorption

The percentage of Cu(II) removed as a function of equilibrium pH and solid concentration using, respectively, sewage sludge ash and pomace ash are shown in Fig. 5a and b. Since the blanks were used to check the background of copper hydroxide precipitates, data points in the cited above figures are the original experimental ones without any correction related to the precipitation effect. The results indicate that the adsorption reaction is greatly affected by pH and adsorbent concentration. In general, the amount of Cu(II) adsorbed increased as solid concentration and pH increased, and sharply reached a 99% removal at pH 7.2, then it remained constant over a wide pH region. The low removal efficiency observed at low pH can be attributed in part to competition between  $\text{H}^+$  and  $\text{Cu}^{2+}$  ion on the surface sites. Indeed, at  $\text{pH} < 2.5$ , the Cu(II) removal was negligible, whereas the removal increased abruptly in the pH range from 2.5 to 5.0 for an adsorbent concentration of  $1 \text{ g L}^{-1}$ . However, as the adsorbent concentration increased to  $10 \text{ g L}^{-1}$ , the abruptly increasing adsorption narrowed to pH between 3.0 and 5.0. Clearly, the above results indicated that increasing adsorbent concentration tended to shift the adsorption edge to the acidic region. Because the copper hydroxide precipitates,  $\text{Cu}(\text{OH})_2(\text{s})$ , were found only at about  $\text{pH} > 5.3$  (see the solid symbols in both Fig. 5a and b),

it confirmed that the removal of Cu by these ashes at  $\text{pH} < 5.3$  was mainly accomplished by adsorption reaction. Up to 95–99% of Cu(II) removal was achieved at  $\text{pH} > 5.3$ , possibly owing to the concurrent precipitation of  $\text{Cu}(\text{OH})_2(\text{s})$  and the adsorption reaction that occurred simultaneously. As shown in Fig. 5a and b, the solution pH is clearly a key factor affecting the adsorption characteristics of Cu(II) onto these ashes. The high dependence on pH for Cu(II) adsorption could be attributed to the surface charge of hydrolyzed adsorbent and the hydrolysis of Cu(II) ion species are both greatly pH-dependent. The pH value of IEP where zero zeta potential occurs is defined as  $\text{pH}_{\text{zpc}}$ . A  $\text{pH}_{\text{zpc}}$  of 2.2 was obtained for both, sewage sludge and pomace ashes. For pure oxides, such as silica, alumina, and ferric oxides  $\text{pH}_{\text{zpc}}$  values are 2.0, 6.7, and 8.5, respectively [21,22]. It is speculated

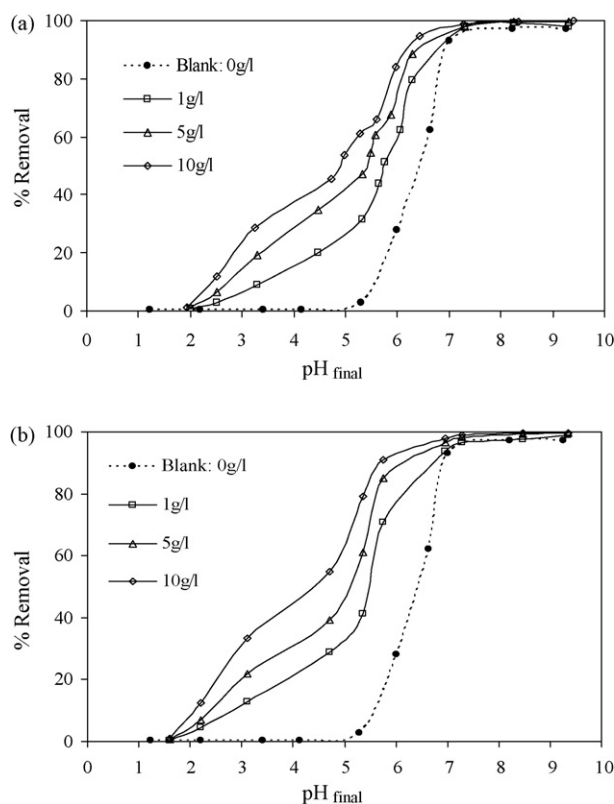


Fig. 5. Effect of pH on the removal of Cu (II) on (a) sewage sludge ash and (b) pomace ash.

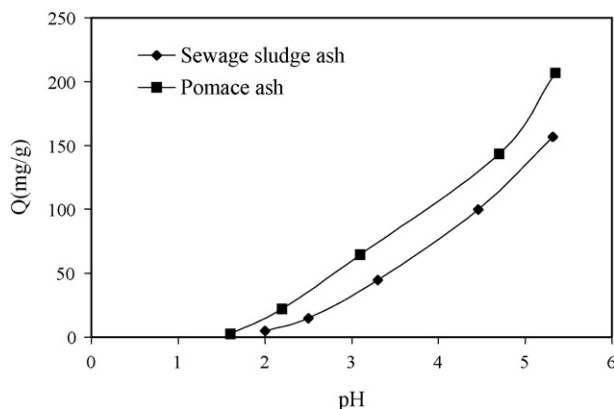
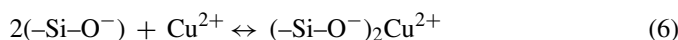
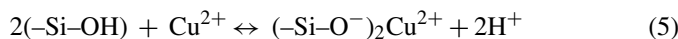
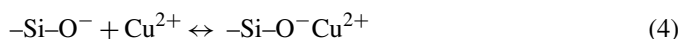


Fig. 6. Amount of Cu(II) adsorbed on sewage sludge ash and pomace ash.

that the lower  $\text{pH}_{\text{zpc}}$  value of sewage sludge and pomace ashes particles is attributed to high silica content (Table 1) versus that of alumina and ferric oxides. The Cu(II) adsorption on sewage sludge and pomace ashes may be attributed to the interaction with surface silica sites with only small contribution from the alumina and iron sites. According to literature [23], the complex reactions of copper ion ( $\text{Cu}^{2+}$ ) with hydrous silicon oxide are listed as follows:



In aqueous solution, surface charge developed from the hydration is an important first step for metal adsorption. Since these adsorbents have a low  $\text{pH}_{\text{zpc}}$ , negatively charged surface should be expected under the pH range investigated. It is noted that the sharply increasing adsorption is in the region of pH 3.0–5.0. In this region, the major adsorbed cationic Cu(II) would be  $\text{Cu}^{2+}$  [13]. As pH increased from 3.0–5.0, it is expected that sewage sludge and pomace ashes surfaces became more negatively charged. Thus more favorable electrostatic attraction forces enhanced cationic copper ions adsorption as pH increased. Consequently, the higher the pH retained, the larger the amount of Cu(II) will be adsorbed as show in Fig. 6. Although pomace ash has low adsorption capacity with regard to the H-type activated carbon such as (EOACC) [19], it can be obtained cheaply in large quantity. Because of its high alkaline nature, sewage sludge ash can be attractive to be used in acidic industrial wastewaters treatment process.

### 3.5. Effect of adsorption temperature

The effect of temperature on the adsorption isotherm was investigated under isothermal conditions in the temperature range of 10–40 °C. Fig. 7a and b shows the temperature dependence of Cu(II) adsorption into sewage sludge and pomace ashes, respectively. The experimental results indicate that the magnitude of Cu(II) adsorption is closely related to the solution

temperature. The adsorption capacity increase when temperature increases from 10 to 40 °C. Agrawal et al. [24] conducted a comparative adsorption study of copper on various industrial solid wastes including sea nodule residue, fly ash and red mud. They found that there was no appreciable effect of temperature on the metal removal on fly ash and red mud. However, other investigations showed that  $\text{Cu}^{2+}$  adsorption on fly ash increased with increasing temperature from 20 to 40 °C [16]. In order to gain insight into the thermodynamic nature of the adsorption process, several thermodynamic parameters for the present system were calculated. The changes of Gibbs free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ) were calculated using the following thermodynamic functions:

$$\Delta G^\circ = -RT \ln K \quad (7)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8)$$

Fig. 8a and b shows the van't Hoff plots of  $\ln K$  versus  $1/T$  and the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  for sewage sludge and pomace ashes, respectively, were determined from the slopes and intercepts. Table 4 lists the calculated thermodynamic parameters. It is noted that all  $\Delta G^\circ$  values shown in Table 4 are negative.

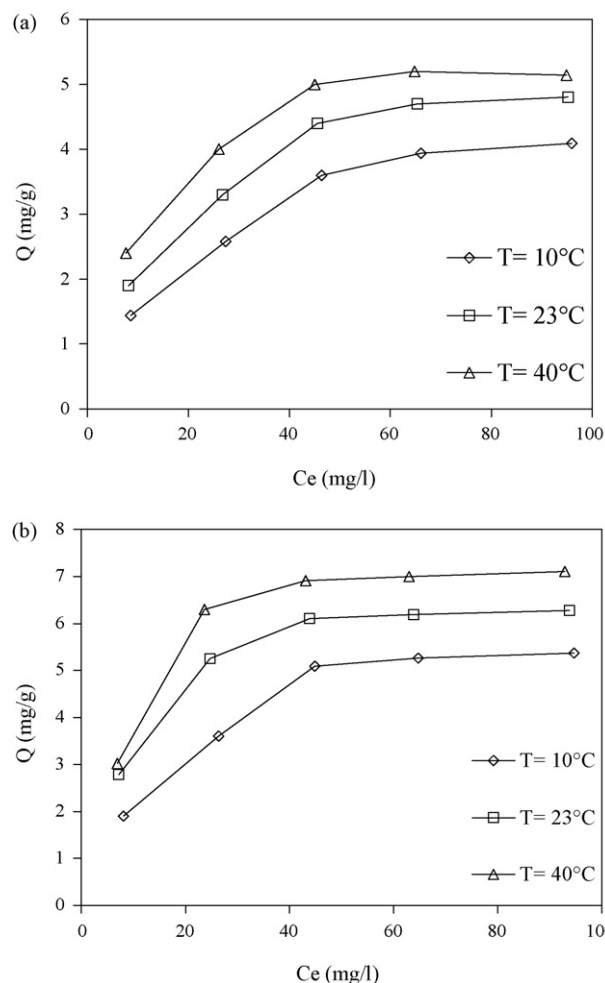


Fig. 7. Cu(II) adsorption isotherm on (a) sewage sludge ash and (b) pomace ash at different temperatures.

Table 4  
Thermodynamic parameters of Cu(II) adsorption on sewage sludge and pomace ashes

Temperature (°C)	Sewage sludge ash			Pomace ash		
	$\Delta G^\circ$ (kcal mol <sup>-1</sup> )	$\Delta H^\circ$ (kcal mol <sup>-1</sup> )	$\Delta S^\circ$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^\circ$ (kcal mol <sup>-1</sup> )	$\Delta H^\circ$ (kcal mol <sup>-1</sup> )	$\Delta S^\circ$ (cal mol <sup>-1</sup> K <sup>-1</sup> )
10	-4.64	4.27	30.6	-4.97	4.33	31.3
23	-4.85	4.27	30.6	-5.23	4.33	31.3
40	-5.13	4.27	30.6	-5.53	4.33	31.3

This suggests that the adsorption process is spontaneous with high preference of Cu(II) for sewage sludge and pomace ashes. The free energy (negative values) increases (from -4.97 to -5.13 kcal mol<sup>-1</sup> in the case of sewage sludge ash and from -5 to -5.53 kcal mol<sup>-1</sup> in the case of pomace ash with an increase of temperature from 10–40 °C, which clearly shows that the process is favorable at higher temperature. Similar results have been demonstrated in the adsorption of metals onto hydrous solids including activated carbon, TiO<sub>2</sub>, alumina, zeolite, and fly ash [25–27]. The changes of energy for physical adsorption are generally smaller than that of chemisorption. The changes of energy for physical adsorption are in the range of 0 to -4.7 kcal mol<sup>-1</sup>, and that of chemical adsorption -19 to -95 kcal mol<sup>-1</sup> [28]. As shown in Table 4, the magnitude of adsorption free energy ( $\Delta G^\circ$ ) ranging from -4.64 to -5.13 kcal mol<sup>-1</sup> for sewage sludge ash

and from -4.97 to -5.53 kcal mol<sup>-1</sup> for pomace ash suggests that the adsorption can be considered as physical adsorption, which was enhanced by the electrostatic effect. As mentioned previously, the negatively charged hydrous ash surface is favorable for the adsorption of cationic Cu(II) ions. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  range, respectively, from 4.27 to 30.6 kcal mol<sup>-1</sup> for sewage sludge ash and from 4.33 to 31.3 cal mol<sup>-1</sup> K<sup>-1</sup> for pomace ash. This suggests that the adsorption is spontaneous and endothermic [29]. The isotherms in Fig. 7a and b show also that the amount of Cu<sup>2+</sup> adsorbed on pomace ash is better than on sewage sludge ash at different temperatures. Since the interaction with surface silica sites is the main responsible for the adsorption of copper ions, the high Cu<sup>2+</sup> retention may be attributed to the high silica content of pomace ash compared to sewage sludge ash particles (Table 1).

#### 4. Conclusion

The present study aimed to investigate the ability of sewage sludge and pomace ash in the removal of Cu(II) from aqueous solutions. The data showed that the solution pH was the key factor affecting the adsorption characteristics. In general, the amount of Cu adsorbed increases as solid concentration and pH increase, and sharply reaches a 99% removal at pH 7.2, then it remains constant over a wide pH region. The marked Cu(II) removal was observed in the acid to neutral region, which can be attributed to the concurrent of Cu(OH)<sub>2</sub>(s) precipitation and the adsorption reactions. In the region of pH3.0–5.0, the Cu(II) removal is controlled by the adsorption and the major cationic copper adsorbed would be Cu<sup>2+</sup>. The equilibrium adsorption could be described by Langmuir adsorption isotherm. The sewage sludge and pomace ashes adsorption capacities of Cu(II) range from 5.71 to 6.98 mg g<sup>-1</sup> and was affected by the pH. The adsorption capacity, however, is not highly affected by temperature in the range 10–40 °C. Experimental results indicate that the adsorption is favorable at higher pH and higher temperature. Values of  $\Delta G^\circ$  ranging from -4.64 to -5.13 kcal mol<sup>-1</sup> for sewage sludge ash and from -4.97 to -5.53 kcal mol<sup>-1</sup> for pomace ash suggest that the adsorption reaction is a physical process simultaneously enhanced by the electrostatic effect. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  range from 4.27 to 30.6 kcal mol<sup>-1</sup> for sewage sludge ash and from 4.33 to 31.3 cal mol<sup>-1</sup> K<sup>-1</sup> for pomace ash, respectively. The experimental studies showed that sewage sludge and pomace ashes could be used as an alternative, inexpensive and effective material to remove high amount of toxic Cu(II) ions from wastewaters.

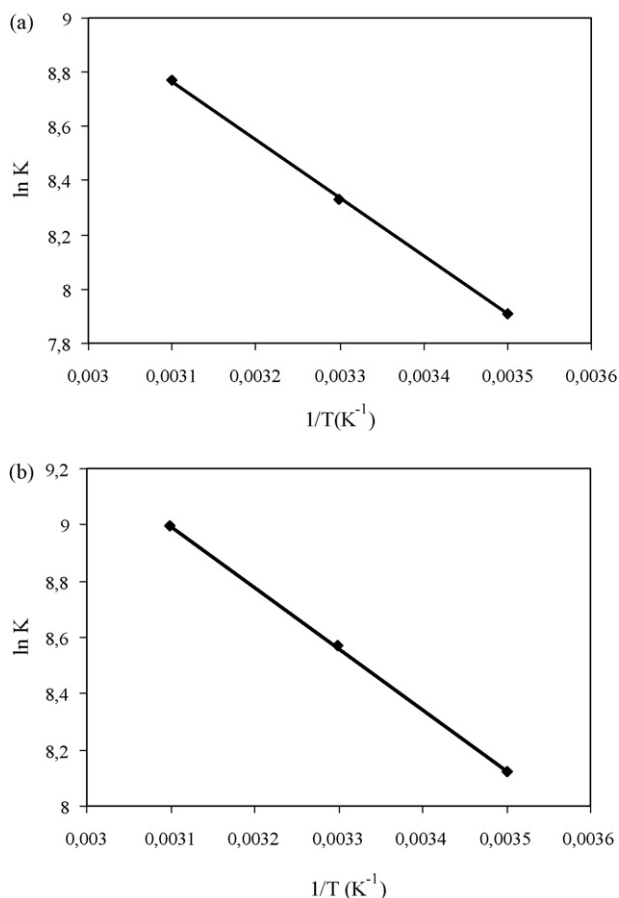


Fig. 8. Relationship between  $1/T$  and  $\ln K$  for (a) sewage sludge ash and (b) pomace ash.

## Acknowledgments

This study was carried out in collaboration between the Tunisian laboratories “Eau Energie et Environnement”, “Laboratoire de chimie industriel I” and the “Eau de Paris” in France. The authors would like to thank Mr. Z. Fakhfakh from Faculty of Science of Sfax for the assistance in MEB, Mr. F. Jamoussi from Research center of water technologies for the X-ray analysis.

## References

- [1] J.C. Dean, F.L. Bosqui, K.H. Lanovette, Removing heavy metals from waste water, *Environ. Sci. Technol.* 6 (1972) 509–518.
- [2] R.T. Camp, *Water and its Impurities*, second ed., Reinhold, New York, 1964.
- [3] M.M. Benjamin, R.S. Slatten, R.P. Bailey, T. Bennett, Sorption and filtration of metals using iron oxide coated sand, *Water Res.* 30 (1996) 2609–2620.
- [4] F.G.A. Vaglisindi, M.M. Benjamin, Redox reactions of arsenic in As-spiked lake water and their effects on As adsorption, *J. Water Supply Res. Technol. Aquat.* 50 (2001) 173–186.
- [5] H. Cho, D. Oh, K. Kim, A study on removal characteristics of heavy metals from aqueous solution by fly ash, *J. Hazard Mater.* 127 (2005) 187–195.
- [6] P.C. Kao, J.H. Tzeng, T.L. Huang, Removal of chlorophenols from aqueous solution by fly ash, *J. Hazard Mater.* 76 (2000) 237–249.
- [7] K.V. Kumar, V. Ramamurthi, S. Sivanesan, Modeling the mechanism involved during the sorption of methylene blue onto fly ash, *J. Coll. Int. Sci.* 284 (2005) 14–21.
- [8] S. Wang, H. Wu, Environmental-benign utilisation of fly ash as low-cost adsorbents, *J. Hazard Mater.* 136 (2006) 482–501.
- [9] J.H. Tay, K.Y. Show, Reuse of wastewater sludge in manufacturing non-conventional construction materials—an innovative approach to ultimate sludge disposal, *Water Sci. Technol.* 26 (1992) 1165–1174.
- [10] J.H. Tay, W.K. Yip, Sludge ash as lightweight concrete material, *J. Environ. Eng. ASCE* 115 (1989) 56–64.
- [11] J.H. Tay, W.K. Yip, K.Y. Show, Clay-blended sludge as lightweight aggregate concrete material, *J. Environ. Eng. ASCE* 117 (1991) 834–844.
- [12] M. Seredych, T.J. Badosz, Removal of copper on composite sewage sludge/industrial sludge-based adsorbents: the role of surface chemistry, *J. Coll. Int. Sci.* 302 (2006) 379–388.
- [13] K.K. Panday, G. Prasad, V.N. Singh, Copper(II) removal from aqueous solutions by fly ash, *Water Res.* 19 (1985) 869–873.
- [14] B. Bayat, Comparative study of adsorption properties of Turkish fly ashes. I: The case of nickel(II), copper(II) and zinc(II), *J. Hazard. Mater.* 95 (2002) 251–273.
- [15] V.K. Gupta, I. Ali, Utilisation of bagasse fly ash (a sugar industry waste) for the removal of copper and zinc from wastewater, *Sep. Purif. Technol.* 18 (2000) 131–140.
- [16] J. Ayala, F. Blanco, P. Garcia, P. Rodriguez, J. Sancho, Asturian fly ash as a heavy metals removal material, *Fuel* 77 (1998) 1147–1154.
- [17] N. Fiol, I. Villaescusa, M. Martinez, N. Miralles, J. Poch, J. Serarols, Sorption of Pb(II), Ni(II), Cu(II) and Cd(II) from aqueous solution by olive stone waste, *Sep. Purif. Technol.* 50 (2006) 132–140.
- [18] F. Kargi, Y. Pamukoglu, Biosorption of copper(II) ions onto powdered waste sludge in a completely mixed fed-batch reactor: estimation of design parameters, *Bioresour. Technol.* 98 (2007) 1155–1162.
- [19] I.D. Harry, B. Saha, I.W. Cumming, Effect of electrochemical oxidation of activated carbon fiber on competitive and noncompetitive sorption of trace toxic metal ions from aqueous solution, *J. Coll. Int. Sci.* 304 (2006) 9–20.
- [20] M. Madhava, A. Ramesh, G. Purna, K. Seshiah, Removal of copper and cadmium from the aqueous solutions by activated carbon derived from Ceiba pentandra hulls, *J. Hazard. Mater.* 129 (2006) 123–129.
- [21] C.P. Huang, E.A. Rhoads, Adsorption of Zn(II) onto hydrous aluminosilicates, *J. Coll. Int. Sci.* 131 (1989) 289–306.
- [22] W. Stumm, J.J. Morgan, *Aquatic Chemistry*, Wiley, New York, 1995.
- [23] S.C. Pan, C.C. Lin, D.H. Tseng, Reusing sewage sludge ash as adsorbent for copper removal from wastewater, *Resour. Conserv. Recycl.* 39 (2003) 79–90.
- [24] A. Agrawal, K.K. Sahu, B.D. Pandey, A comparative adsorption study of copper on various industrial solid wastes, *AIChE J.* 50 (2004) 2430–2438.
- [25] C.H. Weng, Treatment of metal industrial wastewater by fly ash and cement fixation, *J. Environ. Eng. ASCE* 128 (8) (2002) 716–722.
- [26] C.P. Huang, E.H. Smith, Removal of Cd(II) from plating wastewater by an activated carbon process, in: W.J. Cooper (Ed.), *Chemistry in Water Reuse*, vol. 2, Ann Arbor Science Publishers, Ann Arbor, MI, 1981, pp. 355–398 (Chapter 17).
- [27] A.M. Youssef, Th. El-Nabarawy, S.E. Samra, Sorption properties of chemically-activated carbons: 1. Sorption of cadmium (II) ions, *Colloids Surf. A: Physicochem. Eng. Aspects* 235 (2004) 153–163.
- [28] M.J. Jaycock, G.D. Parfitt, *Chemistry of Interfaces*, Ellis Horwood Limited, New York, 1981.
- [29] R.H. Petrucci, Spontaneous change: entropy and free energy, in: *General Chemistry*, fifth ed., Macmillan, New York, 1989, pp. 714–750 (Chapter 20).