

## Kinetic and Thermodynamic Study of the Adsorption of Ni (II) using Spent Activated Clay Mineral

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**Abstract:** Storage of spent bleaching clays (SAC) used in refining and processing of vegetable oil is considered a big problem in the purification of vegetable oil company due to self burner. This study will be contributed to solve this problem by recovering residual vegetable oil contained in spent bleaching clay and reuse the bleaching clay as a low cost adsorbent material. This process will reduce the cost of waste treatment and provide alternative sorbent materials. Removing of Ni(II) from aqueous waste solution using this type of clay has been studied. Characterization of SAC, and treated SAC was reported using Fourier Transform Infra Red (FTIR) and Scan Electron Microscopy (SEM). The adsorption of Ni(II) on treated SAC has been studied as a function of pH, adsorbent dosage, contact time, temperature, and initial Ni(II) concentration. The adsorption amount of Ni(II) ions increased with increasing shaking time and temperature. Adsorption equilibrium was achieved in approximately 180 min. The removal was favored at pH 11 and it was about 99.9%. The kinetics and thermodynamics of adsorption process were evaluated and the data followed pseudo kinetic model. The thermodynamic parameters for the present system including Gibbs free energy of adsorption  $\Delta G^\circ$ , changes in enthalpy of adsorption  $\Delta H^\circ$ , and changes in entropy of adsorption  $\Delta S^\circ$  were calculated using van't Hoff equation. Negative value of  $\Delta G^\circ$  suggests that adsorption is spontaneous. The positive value of  $\Delta H^\circ$  may suggest endothermic process of adsorption.

[N. S. Mahmoud, S. T. Atwa, A. K. Sakr, M. Abdel Geleel **Kinetic and Thermodynamic Study of the Adsorption of Ni (II) using Spent Activated Clay Mineral**] New York Science Journal 2012;5(2):62-68]. (ISSN: 1554-0200). <http://www.sciencepub.net/newyork>. 10

**Keywords:** Activated clay; Adsorption; Heavy metals; Radioactive wastes disposal.

### 1. Introduction:

Activated clay (AC) or so-called activated bleaching earth (ABE), layers silicate mineral, mainly consists of montmorillonites (expanding 2:1 layer structure) activated with sulfuric acid. The main constituents of this clay are SiO<sub>2</sub> (65-75%) and Al<sub>2</sub>O<sub>3</sub> (15-20%) and it has the capacity to remove colored substances and undesirable residues from edible oil. As such, it was used to bleach the crude oil in the refining process to improve the quality of this oil. This process generates a great amount of spent activated clay (SAC) or spent bleaching earth (SBE). After the bleaching operation, the color of AC would change from white to brownish. Generally, it contains approximately 20-30% of oil [1]. It is noted the SAC not only presents a fire hazard (i.e., spontaneous ignition), but also has unpleasant odor. Consequently, the disposal of SAC may pose a serious problem of management and storage [2]. Edible oil refinery factories produce thousands of tonnes/year of SAC. Generally, the residue was disposed of to landfill without any treatment [1].

On the other hand and because of heavy metals toxicity and non-biodegradable nature, the presence of heavy metals in water is becoming a serious environmental problem that attracted the attention of many scientists at present time. Nickel is one of heavy metals with density 8.91 g.cm<sup>-3</sup>. It has a major

impact on environment and human health [3]. The major use of Nickel is in preparation of alloys used in industry especially in nuclear service for its properties. This leads to generate Ni waste in different forms; radioactive and non-radioactive. Removal of heavy metals from wastewater can be achieved by chemical precipitation, ion exchange, reverse osmosis, adsorption, membrane separation, coagulation, electrodialysis, and evaporation. Adsorption is one of the powerful treatment process for the removal of metal ions from wastewater [4-12]. Commonly, various substances such as activated carbon, natural and synthetic zeolites, resins, and clay minerals (aluminosilicate) have been used as adsorbent.

In this study, different types of organic solvents have been used to de-oil spent activated clay SAC. Treated SAC has been used as a new low cost adsorbent to remove Ni(II) from aqueous solutions. It helps to reduce the cost of waste disposal and provide an alternative sorbent. The adsorption of Ni(II) on treated SAC was studied as a function of solution pH, adsorbent dosage, contact time, temperature, and initial Ni(II) concentration. The kinetics and thermodynamics of adsorption process were evaluated in the light of current known models.

## 2. Materials and Methods

### 2.1. Materials

Spent activated clay (SAC) was obtained from Alexandria Company for oils and soap in Alexandria governorate in the northern of Egypt. The commercial virgin activated clay was provided by the edible oil company. This material is montmorillonite activated by sulfuric acid. After the clay was used to remove the color from edible oil, the color of AC would change from white to brownish. It contains 20-30% of oil by weight.

### 2.2. Treatment of SAC

The experiments were performed by washing SAC with different sorts of organic solvents for the purpose of removing oil content and other residues as follows:

1. Prepare a series of polyethylene bottles containing different volumes of Methanol (20 – 30 – 40 – 50 – 100 – 150 – 200 – 450 ml)
2. Add a weighted amount of 20 g of SAC ( $W_1$ ) into the organic solvent.
3. Shake the mixture by using a magnetic stirrer at 300 rpm for 1 hr at room temperature 25 °C.
4. Separate the solution via a 0.45 mm filter paper to collect the Treated-SAC.
5. Record the final weight  $W_2$  of Treated SAC.
6. The percentage of edible oil extracted was determined as below.
7. Amount of oil extracted % =  $[(W_1 - W_2)/(W_1)] \times 100\%$
8. Repeat the steps from (1) to (6) by using different organic solvents: Acetone, Benzene, Toluene, Xylene, Carbon tetra chloride.

### 2.3. Clay mineral characterization

#### 2.3.1. Fourier Transform Infrared Spectrophotometer (FTIR)

Fourier Transform Infrared Spectrophotometer (FTIR) analysis of AC, SAC, and Treated SAC were recorded on FTIR (Nicolet 6700, Thermo Scientific) controlled by OMNIC software by the KBr method; wave numbers in the range of 400-4000  $\text{cm}^{-1}$  with spectral resolution of 8  $\text{cm}^{-1}$ .

#### 2.3.2. Scanning Electron Microscope (SEM)

The morphological characteristics of the SAC, Treated SAC, Ni-absorbed Treated SAC were evaluated by using scanning electron microscope (SEM) (Jeol 5600 LV, Joel, Japan). An electron acceleration voltage of 30 kV was applied for SEM observation. All SEM micrographs of samples were taken at 5000 times magnification.

### 2.4. Adsorption experiments

The Nickel solution was prepared by dissolving a known quantity of AR grade  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (WinLab, UK) in double distilled water and used as a stock solution (1000 mg/L). Ni(II) in the solution before and after adsorption was measuring using Inductively Coupling Plasma (ICP) (Ultima 2 Jobin Yvon, France). The initial metal ion concentration ranged from 20-100 ppm. All experiments were carried out at room temperature 25° C, pH 3.5, adsorbent dosage of the SAC 1 g, and contact time 10 days except as stated otherwise. Standard base of 0.1 M NaOH and acid of 0.1 M HCl were used for pH adjustment. For the effect of pH on adsorption, the pH of solution was maintained at 3, 4, 8, and 11. For the effect of temperature on adsorption, experiments were conducted under different temperature at 20, 25, 40, and 60 °C. For the effect of contact time, the solution was maintained without separation for contact time for 0.5 hr, 1 hr, 3 hrs, 1 day, 3 days, 1 week, 2 weeks, and 3 weeks. For the effect of adsorbent dosage, the experiments were carried out by adding different amount of the Treated SAC into the solution 0.5, 1, 2, 4, and 6 g. The general experimental procedures were described as follows:

1. Prepare a series of 125 mL polyethylene bottles containing 30 ml of Ni(II) concentration (100 mg/L)
2. Add a given amount of the Treated SAC (1 g) into the solution.
3. The mixture was shaken on a magnetic stirrer at 300 rpm for 15 min at room temperature 25 °C.
4. At the end of shaking, record the final pH of the solution.
5. The solution was maintained without separation for contact time 10 days.
6. Separate the adsorbent through a 0.45 mm filter paper to collect the supernatant.
7. Analyze the residual Ni(II) concentration in each of the supernatants using ICP.
8. All data were triplicated and the average values were taken in the data analysis.
9. The adsorption percentage (D) and adsorption capacity or amount adsorbed per unit mass of Treated SAC (q).

$$D = \frac{C_0 - C_f}{C_0} \times 100\%$$

$$q = \frac{(C_0 - C_f)V}{W}$$

Where D is the adsorption percentage (%), q is the adsorption capacity (mg/g),  $C_0$  and  $C_f$  are the initial and final concentration of heavy metal left in solution (mg/L), V is the volume of the aqueous

solution (L), and W is the mass of the Treated SAC (g).

### 3. Results and Discussion

#### 3.1. Properties of SAC

##### 3.1.1. Treatment of SAC

Table 1 outlines the amount of oil removed from SAC by washing it with different organic solvents. The table indicates that the maximum amount of oil removed is 27.08% extracted by using Methanol, while Acetone shows less effectiveness than other

solvents. The efficiency of organic solvents used follows the order Methanol > Toluene > Benzene > Xylene > Carbon tetra chloride > Acetone. Consequently, Methanol is much recommended than other organic solvents in the extraction process of oil from the SAC. This is because it gives a higher yield and a better quality of oil than other organic solvents, low cost, less hazardous than other solvents [13]. After the removal of oil, the color of SAC becomes light.

Table 1. Amount of oil extracted

Volume (ml)/20g	Solvents					
	Methanol	Acetone	Benzene	Toluene	Xylene	Carbon tetra chloride
20	9.17%	0.79%	2.33%	4.78%	1.14%	0.02%
30	13.64%	5.22%	5.79%	6.72%	2.42%	1.02%
40	13.92%	6.98%	7.73%	9.25%	5.99%	2.93%
50	14.39%	7.21%	9.68%	15.15%	9.01%	6.18%
100	19.21%	10.81%	13.03%	18.19%	11.52%	10.59%
150	23.17%	13.58%	17.90%	23.69%	15.37%	14.73%
200	26.23%	13.92%	18.12%	24.41%	16.01%	16.37%
450	27.08%	15.53%	21.98%	24.99%	18.46%	18.37%

##### 3.1.2. Fourier Transform Infrared Spectrophotometer (FTIR)

As seen in Fig. 1, the IR spectrum of SAC mixed with the residue of oily-like materials and other organic materials are completely different from the spectrum of AC as shown on curve b, and the spectrum for Treated SAC is given on curve c. The

spectrum shows a strong band at  $3410\text{ cm}^{-1}$  assigned to OH stretching band. Additionally, an intensive band has been seen at  $1072\text{ cm}^{-1}$ , which attributed to the Si-O stretching vibration, and two bands of amorphous silica at  $790$  and  $470\text{ cm}^{-1}$  are observed [14].

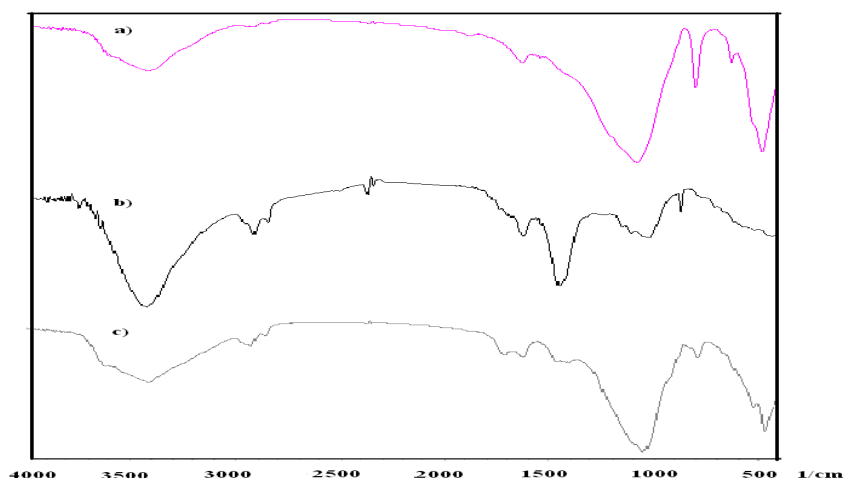


Fig. 1- FTIR spectra of a) AC, b) SAC, and c) Treated SAC

##### 3.1.3. Scanning Electron Microscope (SEM).

The SEM of SAC, Treated SAC, and Treated SAC after adsorption of  $\text{Ni}^{2+}$  ions were presented in Fig. 2. As shown in Fig. 2a, the surface of SAC particles is covered by oily-like materials and it is

almost non-porous [15]. The image Fig. 2b, shows the roughness and irregular layer structure of SAC after treated with methanol, The image Fig.2c. shows the SEM morphology of Treated SAC after adsorption of  $\text{Ni}^{2+}$  ions. There is a clear indication of

adsorbed nickel on Treated SAC as a newly bulky coated layer over the surface via ionic exchange or nonspecific surface adsorption. This phenomenon

implied that the structure of the Ni-adsorbed Treated SAC is different from that of SAC.

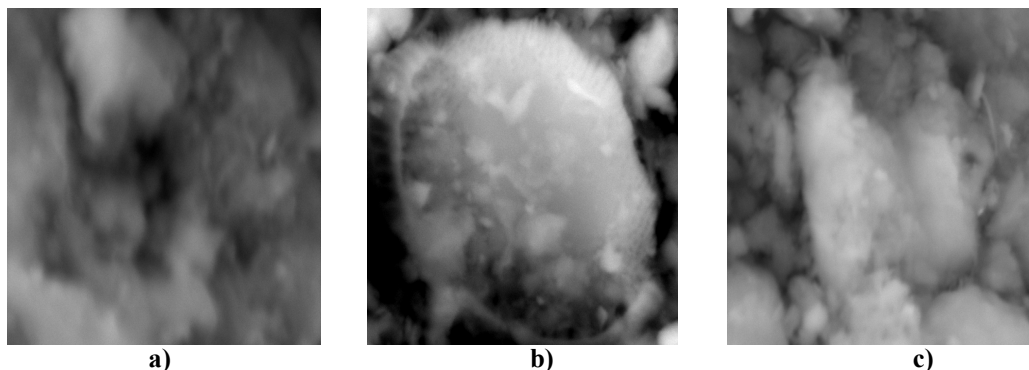


Fig. 2- SEM images of a) SAC, b) Treated SAC, and c) Ni-adsorbed Treated SAC

### 3.2. Effect of contact time.

As seen in Fig. 3, the percentage removal of  $\text{Ni}^{2+}$  ions from aqueous solution increases from 4.75% to 18.32% with the increase of contact time from 30 min to 180 min where it reaches equilibrium. With increasing contact time from 30 min to 3 weeks, the percentage removal of  $\text{Ni}^{2+}$  ions remains the same with no change in value.

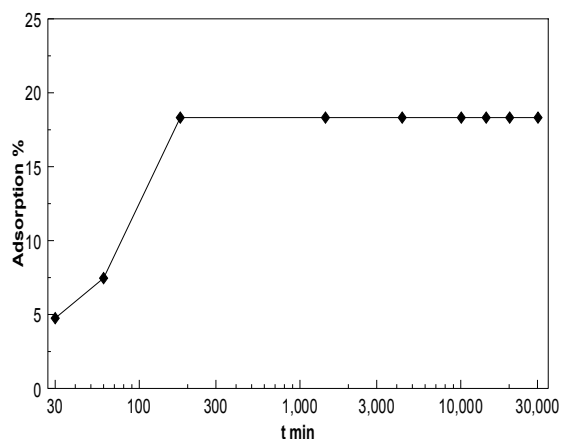


Fig. 3- Effect of contact time on the adsorption percentage of  $\text{Ni}^{2+}$  ( $V=30$  ml,  $W=1$  g,  $C_0=100$  mg/L,  $25^\circ\text{C}$ ,  $\text{pH} 3.5$ )

### 3.3. Effect of pH

The adsorption percentage of  $\text{Ni}^{2+}$  as a function of pH was presented in Fig. 4. The adsorption percentage of  $\text{Ni}^{2+}$  on Treated SAC increased with increasing pH from 3 to 11. Hence, heavy metal adsorption on Treated SAC is critically depending on pH. The adsorption of  $\text{Ni}^{2+}$  increases rapidly in the pH range 3-8. There is no obvious difference in adsorption percentage at pH 8-11. The maximum adsorption percentage of  $\text{Ni}^{2+}$  on Treated SAC at  $\text{pH}=11$  was about 99.9%. The unexpected increase of

adsorption of  $\text{Ni}^{2+}$  may be attributed to its hydroxide precipitation on Treated SAC surface [16].

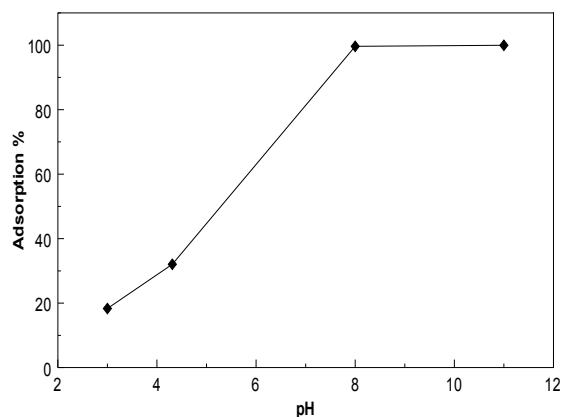


Fig. 4- Effect of pH on the adsorption percentage of  $\text{Ni}^{2+}$  ( $V=30$  ml,  $W=1$  g,  $C_0=100$  mg/L,  $25^\circ\text{C}$ ,  $t=10$  day)

### 3.4. Effect of initial metal ion concentration

The effect of initial concentration of  $\text{Ni}^{2+}$  ions on adsorption percentage was investigated and the results are shown in Fig. 5. The adsorption percentage of removed  $\text{Ni}^{2+}$  increased from 13.03% to 36.33% with increasing the initial concentration of  $\text{Ni}^{2+}$  from 20 to 60 mg/L then decreased to 18.32% with increasing the initial concentration to 100 mg/L. This behavior is due to the adsorption sites on the surface of Treated SAC become saturated and reach equilibrium at initial concentration of  $\text{Ni}^{2+}$  60 mg/L. The increase in the initial concentration of  $\text{Ni}^{2+}$  ions remains in the aqueous solution, which raise the final concentration of nickel.

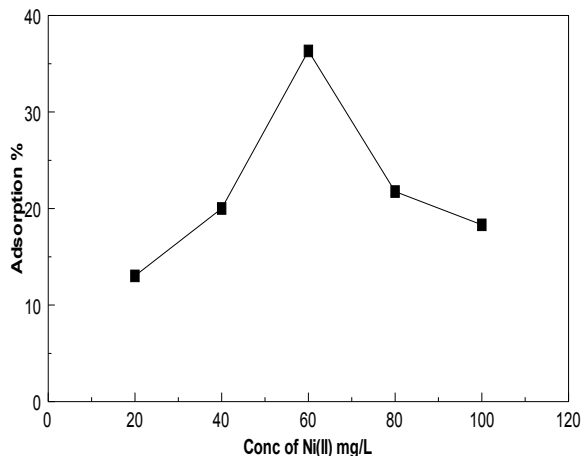


Fig. 5- Effect of initial concentration on the adsorption percentage of  $\text{Ni}^{2+}$  ( $V=30$  ml,  $W=1$  g,  $\text{pH} 3.5$ ,  $25^\circ\text{C}$ ,  $t=10$  day)

### 3.5. Effect of adsorbent dosage

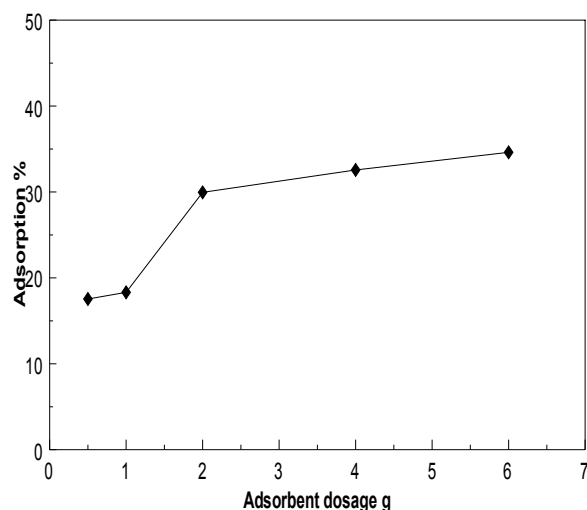


Fig. 6- Effect of adsorbent dosage on the adsorption percentage of  $\text{Ni}^{2+}$  ( $V=30$  ml,  $t=10$  day,  $C_0=100$  mg/L,  $25^\circ\text{C}$ ,  $\text{pH} 3.5$ )

Fig. 6 depicts the influence of adsorbent dosage on  $\text{Ni}^{2+}$  sorption. The percentage adsorption of nickel increased from 17.54% to 34.62% with increase of adsorbent dosage from 0.5 to 6 g. This trend is obvious because as adsorbent dose increases the number of adsorbent particles also increase, that makes the greater availability of exchangeable sites for adsorption [17].

### 3.6. Effect of temperature

The effect of temperature on the adsorption percentage of  $\text{Ni}^{2+}$  ions was studied within range 20-60 °C and the results are shown in Fig. 7. With increasing the temperature range, the adsorption

percentage of  $\text{Ni}^{2+}$  increases from 16.59% to 27.09%. This result implied that the reaction was closely related to energy and it was an endothermic reaction.

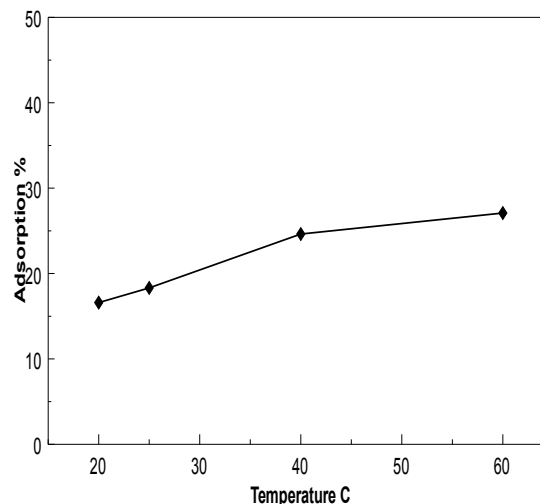


Fig. 7- Effect of temperature on the adsorption percentage of  $\text{Ni}^{2+}$  ( $V=30$  ml,  $t=10$  day,  $C_0=100$  mg/L,  $W=1$  g,  $\text{pH} 3.5$ )

### 3.6. Adsorption kinetics

In order to clarify the adsorption kinetics of  $\text{Ni}^{2+}$  ions on Treated SAC, Lagergren's pseudo-first-order and pseudo-second-order kinetics models were applied to the experimental data.

The linearized form of the pseudo-first-order rate equation by Lagergren is given as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

Where  $q_e$  and  $q_t$  (mg/g) are the amounts of metal ions adsorbed at equilibrium (mg/g) and  $t$  (min), respectively, and  $k_1$  is the rate constants of the equations ( $\text{min}^{-1}$ ). The rate constants  $k_1$  can be determined experimentally by plotting of  $\ln(q_e - q_t)$  versus  $t$ . The plots of  $\ln(q_e - q_t)$  versus  $t$  for Lagergren first-order model and the  $R^2$  value for this model do not fit a pseudo-first-order kinetic model [18]. Experimental data were also applied to the pseudo-second-order kinetic model which is given in the following form:

$$t/q_t = 1/(k_2 q_e^2) + (1/q_e)t \quad (4)$$

Where  $k_2$  ( $\text{min.g/mg}$ ) is the rate constant of the second-order equation,  $q_t$  (mg/g) the amount of adsorption at time  $t$  (min), and  $q_e$  is the amount of adsorption at equilibrium (mg/g).

The model is more likely to predict the kinetic behaviour of adsorption with chemical sorption being the rate controlling step [19]. The linear plots of  $t/q_t$  versus  $t$  for the pseudo-second-order model for the adsorption of  $\text{Ni}^{2+}$  ions on Treated SAC at  $25^\circ\text{C}$  are shown in Fig. 8. The rate constants  $k_2$ , correlation

coefficients of the plots together with the  $q_e$  value is given in Table 2. It is clear from these results that  $R^2$  value equals 1. These results suggest the adsorption of  $Ni^{2+}$  ions onto Treated SAC follows well the pseudo-second-order kinetics [20].

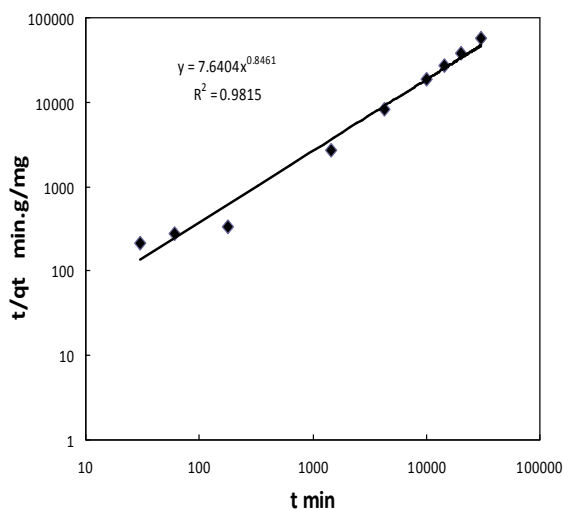


Fig. 8- Pseudo-second-order adsorption kinetics of  $Ni^{2+}$  on Treated SAC.

Table 2. Parameters for adsorption of  $Ni^{2+}$  onto Treated SAC derived from pseudo-second-order.

Pseudo-first-order		Pseudo-second-order		
$q_e$ (mg/g)	$k_1$ ( $min^{-1}$ )	$q_e$ (mg/g)	$k_2$ ( $min.g/mg$ )	$R^2$
0.50643	0.00828	0.533918	0.021558	0.981

### 3.7. Thermodynamic study

The thermodynamic parameters for the present system including Gibbs free energy of adsorption  $\Delta G^\circ$ , changes in enthalpy of adsorption  $\Delta H^\circ$ , and changes in entropy of adsorption  $\Delta S^\circ$  were calculated using Van't Hoff equation.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

$$\Delta G^\circ = -RT \ln k_d \quad (6)$$

$$\ln k_d = (\Delta S^\circ/R) - (\Delta H^\circ/RT) \quad (7)$$

Where  $R$  is the ideal gas constant ( $J/mol.K$ ), and  $T$  is temperature ( $K$ ). The plot of  $\ln k_d$  against  $1/T$  is shown in Fig. 9.  $\Delta H^\circ$  and  $\Delta S^\circ$  values can be obtained from the slope and intercept. The values of thermodynamic parameters are given in Table 3. Negative value of  $\Delta G^\circ$  suggests that adsorption is spontaneous. The positive value of  $\Delta H^\circ$  may suggest endothermic process of adsorption. The endothermic process has been proved before in the experiments of temperature changes. The positive value of  $\Delta S^\circ$  shows the feasibility of adsorption and the increased randomness at the sorbent/solution interface during

the adsorption of metal ions onto Treated SAC [20-22].

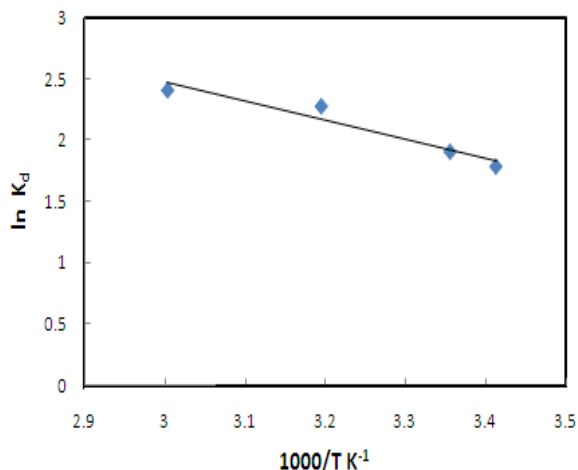


Fig. 9- Van't Hoff plot for  $Ni^{2+}$  adsorption by Treated SAC.

Table 3. Thermodynamic Parameters for the adsorption of  $Ni^{2+}$  by Treated SAC.

Temperature (K)	$\Delta G^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol.K)	$\Delta H^\circ$ (kJ/mol)
293	-4.35289	21.6176	14.550
298	-4.47896		
313	-5.93952		
333	-6.6762		

### 4. Conclusions

The environmental problems related to SAC disposal could be largely solved by removing the oil and coloring materials adsorbed on SAC. The treatment process has cleared the pores of the SAC and has increased the surface area. Furthermore, Treated SAC can be reactivated and reused as adsorbed material while the recovered oil can be used in soap and poultry feed.

The adsorption amount of  $Ni(II)$  ions using this type of clay increased with increasing shaking time and temperature. Adsorption equilibrium was achieved in approximately 180 min. The removal was favored at pH 11 and it was about 99.9%. The kinetics and thermodynamics of adsorption process were evaluated and the data followed pseudo kinetic model. The thermodynamic parameters for the present system including Gibbs free energy of adsorption  $\Delta G^\circ$ , changes in enthalpy of adsorption  $\Delta H^\circ$ , and changes in entropy of adsorption  $\Delta S^\circ$  were calculated using Van't Hoff equation. Negative value of  $\Delta G^\circ$  suggests that adsorption is spontaneous. The positive value of  $\Delta H^\circ$  may suggest endothermic process of adsorption.

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1/2/2012