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2Removal of copper ions from aqueous solution by adsorption using LABORATORIES-modified bentonite (organo-bentonite) Sandy1, Velycia MARAMIS1, Alfin KURNIAWAN1, Aning AYUCITRA1, Jaka SUNARSO2, Suryadi

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Abstract

Equilibrium, kinetic and thermodynamic exhausts of metallurgical, electroplating, printing circuits, aspects of the adsorption of copper ions from an aqueous fertilizer and refining industries. Generally, the concentra- solution using linear alkylbenzene sulfonate (LABORA- tion limit for Cu(II) ions in effluents to be discharged TORIES) modified bentonite (organo-bentonite) are directly into in-land

11surface water is 3.0 mg/L whereas

in reported. Modification of bentonite was performed via drinking water the limit is 0.05 mg/L [1]. Despite the microwave heating with a concentration of LABORA- beneficial effects of trace amounts (μg/L) of copper for TORIES surfactant equivalent to 1.5 times that of the p promoting the enzymatic activities of some microorgan-

3cation exchange capacity (CEC) of the raw bentonite. isms, high concentrations of

this metal ion are undesirable Experimental parameters affecting the adsorption process since they cause irreversible inhibition of some enzymes such as pH, contact time and temperature were studied. o f f r [2]. Moreover, the prolonged oral administration of excess Several adsorption equations (e.g., Langmuir, Freundlich, quantities of copper ions to humans may cause liver Sips and Toth) with temperature dependency were used to damage and acute poisoning. correlate the equilibrium data. These models were Several conventional methods are available for the evaluated based on the theoretical justifications of each treatment of effluents containing copper ions such as isotherm parameter. The Sips model had the best fit for the precipitation, chemical oxidation, ion exchange, reverse adsorption of copper ions onto organo- bentonite. For the osmosis, membrane filtration and electrochemical treat- kinetic data, the pseudo-second order model was superior ment [3]. However, most of these methods are ineffective to the pseudo-first order

model. Thermodynamically, the for removing low concentrations (£10 mg/L) of metal adsorption of copper ions occurs via chemisorption and the ions and result in toxic sludge production which requires process is endothermic ($\Delta H0>0$), irreversible ($\Delta S0>0$) and extra cost for treatment and disposal [4]. On the other hand, nonspontaneous ($\Delta G0>0$). Keywords heavy metal, copper, adsorption, organo- r i n t adsorption is known as a cost effective and promising physiochemical process for this purpose. Numerous studies

> 17**on the removal of** Cu **(II) ions** from wastewater or **bentonite,** temperature dependent **aqueous solutions**

by adsorption

> 12**using different kinds of adsorbents have been reported**

[2,5–7]. To this end, clays 1 Introduction p and clay minerals have emerged as alternative and f inexpensive adsorbents featuring high specific surface areas and high cation exchange capacities as well as good The removal of heavy metals from contaminated effluents mechanical and chemical stability [8].

> 12**is a matter of great interest in the field of environmental** The objective of **this**

work was to evaluate various

> 12**restoration, especially in this era of environmentally**

f equilibrium, kinetic and thermodynamic aspects of the sustainability. Copper is a heavy metal commonly found adsorption of Cu(II) ions from an aqueous solution using in wastewater which primarily originates from the pipeline linear alkylbenzene sulfonate (LABORATORIES) mod- ified bentonite (organo-bentonite). Temperature dependent Received September 9, 2011; accepted November 10, 2011 forms of the Langmuir, Freundlich, Sips and Toth E-mail: suryadiismadji@yahoo.com equations were used to correlate adsorption equilibrium data at various temperatures. Up until now, few studies 2.4 Adsorption experiments have reported the application of these equations to adsorption equilibrium data, especially for metal ions. Adsorption experiments were conducted in a static mode at Most studies on the adsorption of metal ions from three different temperatures (303.15 K, 313.15 K and wastewater or aqueous solutions have used adsorption 323.15 K). A stock solution of copper ions with an initial equations without temperature dependency to correlate concentration of 400 mg/L was prepared by dissolving a adsorption equilibrium data at various temperatures [9– fixed amount of CuSO4$5H2O into 1 L deionized water. 12]. Recently, several adsorption equations with tempera- The adsorption equilibrium experiments were carried out ture dependency were employed to evaluate the equili- by adding various masses of adsorbents (0.1–1.0 g) to a brium data of dye and antibiotic compounds [13,14]. series of conical flasks containing 50 mL of metal solution. Subsequently, the flasks were placed in a water-bath shaker 2 Materials and methods equipped with a temperature controller (Memmert SV- 1422) and shaken at 200 r$min–1 for 1–2 h to reach equilibrium. The metal solution was then centrifuged at The bentonite was Ca-bentonite and collected from a was determined by flame atomic absorption spectro- modification, the bentonite was crushed into powder with a i n t 2.1 Materials 2500 r$min–1 for 10 min to remove the solid particles. The residual concentration of Cu(II) ions in the metal solution mining site in Ponorogo, East Java, Indonesia. Prior to photometer at lmax = 324.6 nm. For adsorption kinetics, the experiments were conducted micro-hammer mill (JANKE and KUNKEL) and sieved as follows: 0.1 g of organo-bentonite was added to a series through a 100/120 mesh screen. The powder was then of conical flasks containing 50 mL of metal solution with

> 10**dried in an oven at** 105 **°C for 2 h. The**

cation exchange initial concentrations of 400

10mg/L. The flasks were then

capacity (CEC) of the bentonite powder was 0.55 meq/g placed in a thermostated shaker and heated from room clay according to ASTM C837-99 procedure. Elemental temperature to the desired temperature (303.15 K, 313.15 K analysis of bentonite was performed with an atomic absorption spectrophotometer (Shimadzu AA6200) with the results as follow: Al2O3 30.71%, SiO2 48.22%, FeO p r or 323.15 K). The shaker was then set at 200 r$min–1 for a given period of time. At regular time intervals, 10 mL of metal solution was removed from the flasks, centrifuged 3.14%, CaO 3.76%, MgO 0.56%, K2O 0.17%, Na2O and analyzed for its residual metal ion concentration. All 1.42% and MnO 0.4%. An analytical grade of linear alkylbenzene sulfonate Sigma Aldrich) was used as the metal ion source. o f f

28experiments were carried out in triplicate with their and used as the

modifying agent in the organo-bentonite Higher pH values were not used since copper ions preparation. Copper sulfate (CuSO4$5H2O; A.R. Grade; precipitate to form Cu(OH)2 at higher pH (more basic n averages used as the result. The effect of pH on the (LABORATORIES) surfactant was purchased from Merck adsorption process was also studied in the pH range of 1–5. condition). To adjust the pH, an appropriate amount of t 0.1 mol$L–1 HCl solution was added. 2.2 Preparation of organo-bentonite The amount of Cu(II) ions adsorbed on a solid surface at equilibrium (qe), in units of mmol/g, can be determined The organo-bentonite was prepared by the following from the following mass balance equation: procedure: 20 g of bentonite powder was mixed with 100 mL of LAS solution with the concentration of LAS ðC0 – CeÞ V equivalent to

31.5 times the CEC of the raw bentonite. The

qe ¼ m , (1) mixture was then subjected to microwave heating (National NN-S327 WF) at a heating power of 700 W for 5 min. The resultant organo-bentonite was

10then washed several times with deionized water and dried in an oven at

p r i

14where C0 and Ce (mmol /L) are the concentrations of Cu(II) ions at initial and equilibrium conditions, respectively, V is the volume of solution (L) and is the mass of

raw m 105°C for 2 h. Finally, the organo-bentonite was crushed, f bentonite or organo-bentonite used (g). sieved and kept in a desiccator until further use. 3 Results and discussion 2.3 Characterizations of adsorbents ometer at 40 kV, 40 mA and a step size of 0.01° using CuKα f 3.1 XRD analysis The XRD patterns of raw bentonite and organo-bentonite were obtained with a Bruker DS Advance powder diffract-

22XRD analysis was performed to characterize the layered structure of the

bentonite before and after modification radiation. The FTIR spectra of the adsorbents were recorded with the LABORATORIES surfactant. The powder XRD with a Shimadzu 8400S spectrometer in the wavenumber patterns of raw bentonite and organo-bentonite (figures not range of 500 to 4000 cm–1, using a KBr disk procedure. shown here) had reflection peaks at about 2θ = 5.12° and 4.34°. These peaks correspond to the basal spacing, d(001) the interlayer of bentonite render a positive effect on the and represent the 2:1 layer thickness of smectites, with adsorption of copper ions promoting the electrostatic values of 1.724 and 2.012

nm for raw bentonite and interactions between the negatively charged solid surface organo-bentonite, respectively. The increased basal spa- and the metal cations. cing

> 3**in organo-bentonite indicates that** the LAS **molecules**

In the pH range of 3–6, the amount of metal ions

> 3**were partially intercalated into the interlayer spacing of**

adsorbed remains fairly constant. As previously men- bentonite thus lengthening its 2:1 interlamellar distance. tioned, the pH study was limited to pH < 6.0 due to precipitation of copper ions as Cu(OH)2 at higher pH. For 3.2 FTIR analysis this reason,

> 11**pH 5 was selected as** the **optimum** condition **for** subsequent **studies**

on copper ion removal. Table 1 presents the vibrational modes of various functional groups on the surface of raw bentonite and 3.4 Adsorption isotherms organo-bentonite from 500 to 4000 cm–1. The band at 3630 cm–1 indicates an O–H stretch in the At equilibrium conditions, there is a defined relationship t silanol (Si–OH) or aluminol (Al–OH) groups. Asymmetric between the solute concentration in solution and that in the and symmetric C–H stretching bands for the (– CH2)n in adsorbed state (i.e., the amount of solute adsorbed per unit the LAS carbon chains on the organo-bentonite were seen mass of adsorbent). The correlation of adsorption equili- at 2855–2925 cm–1. The bending vibration at 1460 cm–1 is brium data with either a theoretical or an empirical ascribed to the deformation of – CH2, which is also equation is essential to describe adsorption behavior as observed in the organo-bentonite. The slight shift in the well as to predict its extent. Different adsorption models, f p r i n peak at 780 cm–1 (raw bentonite) to 795 cm–1 (organo- that were initially developed for gas phase adsorption and bentonite), which is the characteristic of the quartz Si–O later extended to liquid phase adsorption, have been stretch, denotes a change in structure in the interior of the successfully applied to correlate adsorption equilibrium raw bentonite during microwave heating. data for various systems. Since adsorption is a tempera- ture-dependent process, it is logically assumed that 3.3 Effect of pH adsorption models also exhibit temperature dependency. To this end, several adsorption models in their tempera- The

> 6**effect of pH on the adsorption of Cu(II) ions onto**

ture-dependent forms were used to evaluate their applic- organo-bentonite is shown in Fig. 1. adsorbate molecules so they can penetrate into the solid is independent of the occupancy of its neighboring sites o f ability to the equilibrium data for the adsorption of copper From Fig. 1, it can be seen that as the pH increases from ions onto organo-bentonite at various temperatures. 1 to 3, the amount of copper ions adsorbed increases from A Langmuir model was developed based on three 0.03 to 0.07 mmol/g. In acidic solutions, the adsorption of assumptions: 1) adsorption is limited to monolayer cover- copper ions is not favored due to the competitions with H+. age; 2) all solid surface sites are alike and 3) each surface Increasing pH reduces the concentration of hydrogen ions site on the solid can only accommodate one adsorbed atom t in the metal solution and thus facilitates the mobility of the and the ability of a molecule to be adsorbed on a given site surface. Increasing pH also leads to more negatively [15]. The Langmuir model is expressed mathematically as: charged surface sites on the solid. These sites are associated with deprotonated silanol (≡Si–O–) or aluminol Ceqmax KL (≡Al–O–) species. This in turn, results in an electrostatic p r i n qe ¼ 1 þ CeKL , (2) interaction between the Cu(II) ions and these species. Moreover, the presences of LABORATORIES anions at where qe is the amount of Cu(II) ions adsorbed under f equilibrium conditions (mmol/g); qmax is the maximum Table 1 FTIR assignments of raw bentonite and organo-bentonite Assignments Wavenumber /(cm–1) Raw bentonite Organo-bentonite Al–OH or Si–OH stretch 3630 3624 Asymmetric C–H stretch of (–CH2)n 2925 (symmetric vibration) H–O–H bend f – 2855 1640 1647 C–H in plane binding (for alkyl groups) – 1465 O–H bend bounded with 2Al3+ 948 955 Si–O bend of quartz 780 795 where KF0 is the adsorption affinity of the solute at 298.15 K; A0 is a characteristic of the

adsorption potential (J/mol) and α is a constant. The Sips or Langmuir-Freundlich equation is a three-parameter isotherm model that was proposed to circumvent the impossibility of a continual increase in the adsorbed amount as the adsorbate concentration increases, which is encountered in the Freundlich model [15]. The Sips equation has the form: qe ¼ qmax ðKSCeÞn 1 1 þ ðCeKSÞn 1 : (8) The temperature-dependent forms of KS and n are expressed below: Fig. 1

> 6**Effect of pH on the adsorption of Cu(II) ions onto**

organo- bentonite (Operation conditions: C0 = 400 mg/L, adsorbent mass = r i n t KSðTÞ ¼ KS0exp Q T0 – 1 T , (9) 0.8 g, t = 303.15 K) RT

> 33**adsorption capacity of the adsorbent** (mmol **/g),** corre- nSðTÞ ¼ **1 1**

(10) sponding to monolayer surface coverage; and KL is the adsorption affinity constant or the Langmuir constant n þ η 1 – T0 , 0 T (L/mmol). The temperature-dependent forms of qmax and KL are as follows [15,16]: f qmaxðTÞ ¼ q0exp½δðT –T0ÞŠ, value of nS at 298.15 K and η is a constant. The KLðTÞ ¼ KL0exp RT f p where KS is the affinity coefficient (L/mmol); nS is a parameter characterizing the system heterogeneity; KS0 is (3) the adsorption affinity at 298.15 K (L/mmol); n0 is the Q temperature dependent form of qmax is given in Eq. (3). : (4) The Toth equation is another three-parameter isotherm model that describes the adsorption behavior in hetero- Here, q0 is the adsorption capacity at the reference geneous systems. The Toth equation with its temperature temperature (T0), taken here as 298.15 K (mmol/g); δ is a dependency has the forms: parameter associated with the expansion coefficient of the adsorbate ions; KL0 is the adsorption affinity at 298.15 K o n t qe ¼ ½1 þ ðbTCeÞnTŠnT qmax bTCe 1 , (11) (L/mmol); Q

> 5**is the heat of adsorption** (J **$mol–1)** and **R is the** universal **gas constant (8.314 J$mol–1$K–1).**

A Freundlich model was proposed on the assumption bTðTÞ ¼ b0exp Q that the solid surface is heterogeneous in the sense that the i T0 – 1 , (12) RT T adsorption energy is evenly distributed and the surface topography is patch-wise [15]. The Freundlich model can be expressed mathematically as follows: nTðT Þ ¼ n0 þ η 1 – T0 T : (13) f p 1 qe ¼ KFCen: r (5) Here, bT is the affinity coefficient (L/mmol); nT is a Here, KF is the Freundlich parameter associated with the characteristic parameter for the system heterogeneity; b0 is adsorption affinity [(mmol/g)$(mmol/L)–n]; and n is a the adsorption affinity at 298.15 K (L/mmol); n0 is the parameter that characterizes the system heterogeneity. The f value of nT at 298.15 K and η is

> 32**a constant. The values of parameters** KF **and** n **are**

temperature-dependent parameters bT and nT are specific for specific adsorbent-adsorbate with their mathematic equations as follows [15]: pairs. Figures 2–5 show the isotherm plots of the adsorption 1 n ¼ RT A0 , (6) equilibrium data at various temperatures fitted to Lang- muir, Freundlich, Sips and Toth models respectively. The model parameters were obtained by non-linear least squares fitting of the adsorption models to the experimental KFðTÞ ¼ KF0exp – A0 αRT , (7) data and the results are summarized in Table 2. For this purpose, the sum of squares of the errors was employed as are reasonable and comparable to the typical values obtained for the adsorption capacity of clay-based adsorbents [17–21]. The next important parameter used to evaluate the adequacy of the model is the heat of adsorption (Q). An inconsistent Q value (with respect to the experimental data) was observed for the Toth model. The fitted result for the Q parameter obtained by the Toth model leads to a positive Q value, indicating an exothermic process. In contrast, the experimental data in Fig. 5 shows that the adsorption capacity increases with temperature, denoting an endothermic process and indicating that thermal energy is required to make the process more favorable. Due to this inconsistency, the Toth model fails to give the best correlation with the experimental data. Fig. 2

2Equilibrium plot of the adsorption of Cu(II) **onto organo-**

i t The δ parameter relates closely to the expansion coefficient of the adsorbate ions. Its magnitude is normally on the order of 10–3 K–1 [16]. Accordingly, the δ values n bentonite at various temperatures–Langnuir model obtained from the nonlinear least squares fitting method with the Langmuir and Sips equations are consistent and the objective function to be minimized. thus it can be assumed that for this parameter, both At a glance, Figs. 2–5 demonstrate that the Langmuir, equations provide adequate correlations with the experi- Sips and Toth models can all represent the experimental mental data. data well (substantially better than the Freundlich model). r Nevertheless, to confirm the validity of the models in measure of the extent of interactions between the representing the adsorption data, the theoretical justifica- adsorbates and the solid surface. High values of affinity tions of each model's parameters need to be examined. f p The affinity parameter at 298.15K (KL0 and KS0) is a lead to an increase in the amount of solutes covering the The q0 values of organo-bentonite (0.29–0.34 mmol/g) solid surface. The fitted value of the affinity parameter obtained from the fitted Langmuir, Sips and Toth equations obtained from the Langmuir model is unreasonably high, Table 2 Fitted temperature dependent parameters for several adsorption equations for the adsorption of Cu(II) ions onto organo-bentonite Adsorption equation f Parameter t Value Langmuir o q0 /(mmol$g–1) 0.285 KL0 /(L$mmol–1) 1036.8 Q/(kJ$mol–1) – 8.94 δ /(K–1) Freundlich n 9.5 10–3 KF0 /[(mmol/g)$(mmol/L)–n] 0.0061 – 0.0016 p α/A0 A0 /(kJ$mol–1) 9.57 Sips q0 /(mmol$g–1) r i 0.326 f KS0 /(L$mmol–1) 17.59 Q /(kJ$mol–1) – 13.67 δ /(K–1) 7.8 10–3 n0 1.458 H 1.371 Toth f q0 /(mmol$g–1) 0.3441 b0 /(L$mmol–1) 59.205 Q /(kJ$mol–1) 4.02 δ /(K–1) 6.7 10–3 n0 0.5443 H 1.8025 especially considering the fact that the adsorption process occurs in the liquid phase. The Sips model, on the other hand, provides a more reasonable affinity value for the metal-ion-clay adsorbent system. Therefore, the only model which satisfies all theoretical justifications of the isotherm parameters is the Sips model. 3.5 Adsorption kinetics n In designing industrial adsorption systems, it is crucial to understand the kinetics of the adsorption process, espe- cially the adsorption mechanism and the rate-controlling p i step. The latter information is generally required to optimize the operating conditions for full-scale batch t metal removal processes. To this end, several kinetic Fig. 3

2Equilibrium plot of the adsorption of Cu(II) **ions onto organo-bentonite at various temperatures–Freundich model**

r models are available and the pseudo-first order and pseudo-second order are the most widely used for representing kinetic data. The first order rate equation, also known as the pseudo- first order model was first proposed by Lagergren in the 19th century [22]. This model has the form: ddqtt ¼ k1ðqe – qtÞ, (15) where k1

9is the rate constant of the **pseudo-first order** model f f **(min–1). Integration of Eq.** (15) **with boundary conditions** of **t = 0,** q = 0 and **t = t, q**

= qt and rearrangement give: o qt ¼ qe½1 – expð – k1tÞŠ: (16) n The pseudo-second order model is commonly used when the rate of the adsorption/desorption process controls the overall sorption kinetics. The mathematical expression of this model was first developed by Blanchard et al. [23]. The pseudo-second order model was derived on the basis t Fig. 4

2Equilibrium plot of the adsorption of onto Cu(II) **organo-**

of the adsorption capacity of the solid phase, and is bentonite at various temperatures–Sip smodel f r i expressed as follows: p ddqtt ¼ k2ðqe – qtÞ2: (17) Here,

31k2 is the rate constant for the **pseudo-second order model (g$** mmol **– 1$min–** 1). Integration of **Eq.** (17) with **boundary conditions** of t = **0,** q = 0 and **t = t,**

q = **qt**

and rearrangement give: 1 1 f qe – qt ¼ qe þ k2t: (18) The kinetic parameters for the adsorption of Cu(II) ions onto organo-bentonite were calculated by nonlinear fitting of the models to the experimental data and the results are presented in Table 3. Plots of the kinetic experimental data and the fitted pseudo-first and pseudo-second order models are shown in Figs. 6 and 7, respectively. The pseudo-second order Fig. 5

2**Equilibrium plot of the adsorption of** Cu(II) **ions onto**

model is a better fit than the pseudo-first order, which is organo-bentonite at various temperatures–Toth model indicated by the higher correlation coefficients (R2).

7**Table 3** Fitted **kinetic parameters for** the **adsorption of** Cu(II) ions **onto** organo-bentonite **T /K qe,exp** /(mmol **$g–1) Pseudo-first order Pseudo-second order qe/(** mmol **$g–1) k1/(min–1) R2 qe/(** mmol **$g–1) k2/(g$** mmol **–1$min–1)**

R2 303.15 0.2972 0.2903 0.1612 0.9486 0.3074 1.1271 0.9849 313.15 0.3243 0.3175 0.1795 0.9249 0.3335 1.2656 0.9928 323.15 0.3632 0.3550 0.1906 0.9166 0.3710 dependency on the initial solute concentration [24]. Moreover, temperature also plays an important role in i the adsorption kinetics since a change in temperature results in a change in equilibrium conditions. This is t 1.2868 0.9933 be regarded as a time-scaling factor due to its strong evidenced by the increase in qe from 0.3074 to 0.3710 r mmol/g when the temperature is increased from 303.15 K to 323.15 K. A higher qe value also translates to a higher n value of k2, resulting in a faster uptake of metal ions and a shorter time to reach an equilibrium state. Heating, therefore, promotes the adsorption process. 3.6 Thermodynamic studies Fig. 6 Kinetic plot for the adsorption of Cu(II) ions onto organo- (ΔH0), entropy (ΔS0) and Gibb's free energy (ΔG0) are bentonite at various temperatures f f p Thermodynamic parameters, i.e., changes in enthalpy also important to completely evaluate the Cu-adsorption process. The calculation of the above thermodynamic parameters was conducted using the van't Hoff equations o below: ΔG0 ¼ ΔH 0 – T ΔS0, (19) i t ΔG0 ¼ –RTlnKD: (20) Equations (19) and (20) can also be written in a linear form r with respect to KD and 1/T as follows: n lnKD ¼ ΔS0 ΔH0 R – RT , (21) where KD is the thermodynamic distribution coefficient representing the equilibrium concentration of the solute on the solid surface (mmol/g) and the equilibrium concentra- tion in the metal solution (mmol/g); ΔS0 and ΔH0 are the Fig. 7 Kinetic plot

32**for the adsorption of Cu(II)** ions **onto** organo- bentonite **at various temperatures**

standard entropy

9**(kJ$mol–1$K–1)** and the **standard enthalpy** changes (kJ **$mol–1),** respectively; ΔG0 **is the**

standard f f Gibb's

33**free energy change (kJ$mol–1)** and **R is the**

In addition, the fitted

25**values of qe** in **the pseudo-second** p **order model are** consistent with **the experimental qe**

values. universal gas constant (8.314 10–3 kJ$mol–1$K–1). These results indicate that the adsorption
process obeys a The

7**values of ΔH0 and ΔS0 were** obtained **from the slope**

pseudo-second order model. In most cases, this model can and intercept of a linear plot of lnKD vs. 1/T as
shown in Fig. 8. The thermodynamic parameters of the adsorption predict very accurately the actual amount
adsorbed at process are summarized in Table 4. The positive ΔH0 value equilibrium due to its small
sensitivity to random indicates the adsorption process is endothermic, which is experimental error.
consistent with the previous equilibrium and kinetic Generally, the value of k2 strongly depends on the
studies. The endothermic nature of the process is due to operating conditions, to the extent that this
parameter can the strong interactions between the solid and the Cu(II) Table 4

21**Thermodynamic parameters for the adsorption of** Cu(II) ions **onto** organo-
bentonite **T /K ΔG0/(J $mol–1) ΔH0 /(kJ$mol–1) ΔS0 /(J$mol–1$K–1)**

R2 303.15 2005.54 313.15 1346.82 323.15 688.1 21.96 65.87 0.9833 lnk2 ¼ lnA – RT Ea : (22) Here, A is
the temperature-independent Arrhenius constant and Ea is the activation energy (kJ$mol–1). The activation
energy can be determined from the slope of an Arrhenius plot of lnk2 vs. 1/T. This plot (not shown here)
gave Ea = t + 40.2 kJ/mol,

17**indicating that adsorption of** Cu **(II) ions onto** organo **-bentonite**

occurs via chemisorption. 4 Conclusions Organo-bentonite was prepared via modification of o f f p r i n
bentonite using linear alkyl benzene sulfonate surfactant via microwave heating. Adsorption experiments
were

11**Fig. 8 van't Hoff plot** for **adsorption of Cu(II)** ions **onto**

organo- carried out in a static mode at various temperatures bentonite (303.15 K, 313.15 K and 323.15 K)
and at pH 5. For correlations of the adsorption equilibrium data, the ions, where energy is required for the
initial stripping of the temperature dependent forms of the Langmuir, Freundlich, metal ions from their
hydration shells [2]. Sips and Toth equations were employed. Based on the Furthermorpe, one of the
possible adsorption mechan- theoretical justifications of each model parameter, the Sips isms between
Cu(II) ions and organo-bentonite involves equation demonstrates the best representation of the the
exchange of metal ions with H+ ions. This requires an adsorption equilibrium data. For the kinetic data
correla- input of energy for the cleavage of the hydroxyl group tion, the pseudo-second order model was
superior to the hydrogen bonds prior to the cation exchange. pseudo-first order model. Thermodynamically,
the adsorp- The positive ΔS0 value reveals the increased degree of tion of Cu(II) ions onto organo-bentonite
occurs via t

23**randomness at the solid-solution interface during the** chemisorption and **the
process**

is endothermic, irreversible adsorption process. This is probably due to the structural and non-spontaneous.
changes in the solid caused by the intercalation of metal itorannss,ittihoenrealnedasethoef
dhiystdrriabtuetdiownaotefr rdoutaritniogntahleamndetatrlainosnlas'- References tional energies among the
solute molecules in the adsorbed i n state [25]. The positive ΔG0 values indicate the process is 1.

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