ADSORPTION OF COPPER FROM AQUEOUS SOLUTIONS BY USING NATURAL CLAY

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Abstract: In this study, removal of copper (Cu^{2+}) from aqueous solutions is investigated using a natural clay. During the removal process, batch technique is used, and the effects of pH, clay amount, heavy metal concentration and agitation time on adsorption efficiency are studied. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms are applied in order to determine the efficiency of natural clay used as an adsorbent. Results show that all isotherms are linear. It is determined that adsorption of Cu^{2+} is well-fitted by the second order reaction kinetic. In addition, calculated and experimental heavy metal amounts adsorbed by the unit clay mass are too close to each other. It is concluded that natural clay can be used as an effective adsorbent for removing Cu^{2+} from aqueous solutions.

Keywords: Natural clay; Copper; Zinc; Freundlich isotherm; Langmuir isotherm; D–R isotherm; Reaction kinetic

Introduction

Water is usually not occur at the locations & times where & when it is most needed. As a result, it becomes one of the most strategic raw materials. The pressure of increasing population, urbanization, lack of environmental awareness, lack of implementation of environmental rules and regulations can cause surface water and groundwater pollution. Water pollution is harmful for human and animal health.

Copper (Cu) is an essential substance to human life, however in high doses it is toxic and can cause anemia, liver and kidney damage. Cu metal contamination exists in water from many industries such as electronic, plating, mining and glass coloring. It is unfortunate that Cu is persistent which is not easily metabolized or breakdown in the environment. Various methods exist for the removal of Cu from water such as ion-exchange, reverse osmosis, adsorption and chemical settling **(Cheremisinoff, 1995) (Lin & Juang, 2002)**. Among them adsorption is the most effective and widely used method. Activated carbon and chelation resins are the most common adsorbents used in water treatment all over the world **(Veli & Öztürk, 2005)**. However, activated carbon and commercial chelating resins are expensive materials, therefore many studies have been done in order to find out effective and low cost adsorbents.

The present work investigates the feasibility of the low-cost adsorbent kaolinite clay for the removal of Cu from water. In the study, the effects of several factors such as pH, concentration of solution, clay mass and contact time on copper removal efficiency were examined.

Huge amounts of clays are available in the Arab Republic of Egypt. Alkatamya clay is a local term that refers to natural clay mineral from Wadi Hagoul area in Egypt. Wadi Hagoul clays were used in the past as friendly building materials compared to Portland and cements.

1.   Materials and methods

Clay samples were obtained from Wadi Hagoul, Suez, Egypt. The chemical composition of adsorbent is provided in (Tab.1). Adsorption of Cu with clay was carried out in a batch reactor. 1000 mg/L of Cu stock solution was prepared by dissolving 3.8 g of $Cu(NO_3)_2 \cdot 3H_2O$ in 1 L distilled water. Standard Cu solution ranging between 10 and 300 mg/L were prepared by diluting the stock solutions. Samples was determined to be 50 mL. pH adjustments were carried out using 0.1N HCl and 0.1N NaOH. 200 rpm stirring rate and 25 °C temperature were applied in the shaker. Samples with clay content in the range of 0.05− 0.08 g were taken from the shaker at regular contact time intervals and the clay was separated by filtering.

Tab. 1. XRF Analysis of Clay (%)

Oxides	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	K_2O	Na_2O	P_2O_5	L.O.I	Total
Amountn(%)	49.79	13.77	0.17	9.98	1.1	2.48	1.27	0.75	2.15	18.48	99.94

The equilibrium isotherms for Cu was obtained by performing batch adsorption studies. Solutions of 100 mg/L concentration were adjusted to optimum pH values and clay amounts ranging between 0.05 and 0.8 g were added to solutions. The adsorbed heavy metal amount (q_e) per unit absorbent mass was calculated as follows:

$$q_e = \frac{(C_o - C_e)V_L}{W_g} \qquad\qquad (1)$$

Where, C_o is the initial heavy metal concentration, C_e is the concentration of heavy metal at equilibrium (mg/L), W_g is the clay mass (g) and V_L is the solution volume (L).

2.   Results and discussion

2.1 Evaluation of the adsorption capacity

2.1.1 Effect of pH

In the experiments, clay content was kept constant (0.05 g) and agitation time was determined to be 24 h at 200 rpm. The results are shown in (Fig.1). The highest removal efficiency in the Cu adsorption with natural clay was obtained at pH 6. At lower pH values, the adsorption efficiency was decreased.
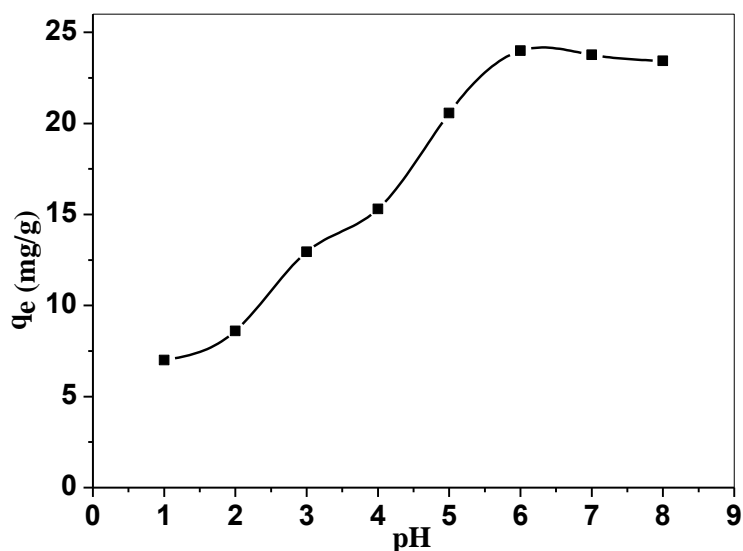

Fig. 1. Effect of pH on the removal of Cu^{2+} by natural clay. Initial metal concentrations 50 mg/L, clay dosage 0.05 g/100 mL, contact time 24 h.

2.1.2 Effect of clay dosage

In the Cu removal, it is seen that the adsorption efficiency increases as the clay amount increases (Fig. 2). The increase in the efficiency can be explained by the increasing surface area where the adsorption takes place. As seen in (Fig. 2), optimum clay dosages that can be used in Cu is 0.5 g/50 mL.
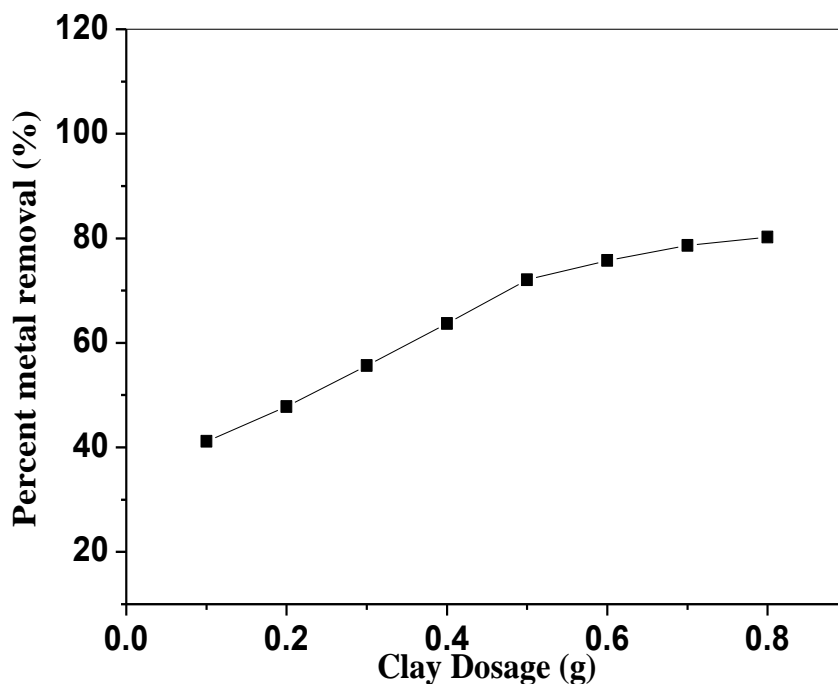
Fig. 2. Effect of clay dosage on the removal of Cu^{2+} by natural clay. Initial metal concentrations 100 mg/L, pH 6, contact time 24 h.

2.1.3 Effect of metal concentration

The adsorption efficiency increased to a certain level and remained stable as the concentration increased. Following the saturation on the surface where the adsorption takes place, no more metal ions can be adsorbed. The optimum metal concentration was determined as 150 mg/L. The results obtained from the experimental studies are shown in (Fig. 3).
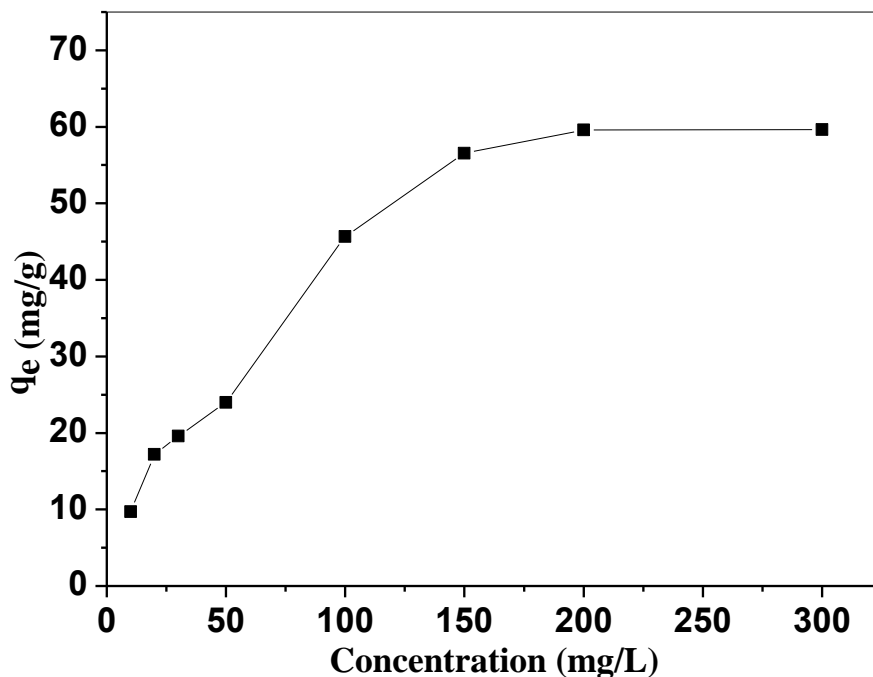

Fig. 3. Effect of metal concentration on the removal of Cu^{2+} by natural clay. Clay dosage 0.05 g, pH 6, contact time 24h.

2.1.4 Effect of agitation time

As shown in (Fig.4) on the natural clay the equilibrium adsorption was established rapidly within 120 min, indicating that the initial adsorption was fast and maximum uptake was reached within 175 min for Cu, thereafter, the amount of adsorption remained almost constant. This was due to the decrease of adsorption sites on the clay which gradually interacted with the metal ions, but the adsorption rate depends on the metal ions which transported from the bulk liquid phase to the actual adsorption sites **(Yu et al., 2000)**.
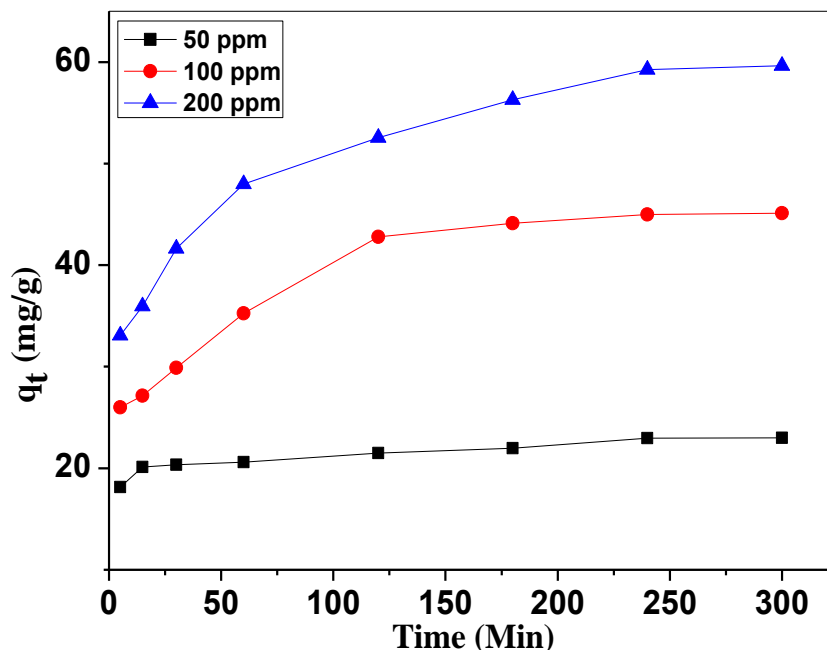

Fig. 4 Effect of contact time on the removal of Cu2+ natural clay. Clay dosage 0.05 g/50mL, pH 6.

2.2 Adsorption isotherms
2.2.1 Langmuir isotherm

Langmuir isotherm models the single coating layer on adsorption surface **(Langmuir, 1918).** This model supposes that the adsorption takes place at a specific adsorption surface. The attraction between molecules decreases as getting further from the adsorption surface **(Ünlü & Ersoz, 2006)**. Langmuir isotherm can be defined according to the following formulas:

$$q_e = \frac{q_{max}bc_e}{1+bc_e} \tag{2}$$

Where, q_e is the amount of adsorbed heavy metal per unit clay mass (mg/g), q_{max} is the monolayer capacity, b is the equilibrium constant and c_e is the equilibrium concentration of the solution (mg/L).

Eq. (2) can be written in the following linear form in Eq. (3):

$$\frac{c_e}{q_e} = \frac{1}{bq_{max}} + \frac{1}{q_{max}}c_e \tag{3}$$

The results obtained from the empirical studies were applied to Langmuir isotherm. The dependence of $\frac{c_e}{q_e}$ from c_e was obtained by using empirical results for the natural clay (Fig.5).
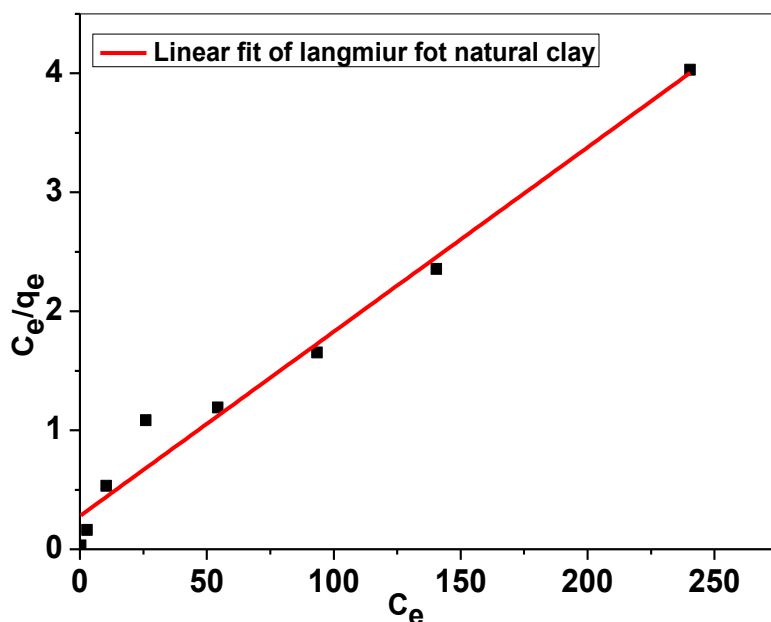
Fig. 5 Langmuir isotherms for the natural clay.

The data obtained from the various plots as summarized in (Tab. 2) show that adsorption of Cu follow the Langmuir isotherm model very well.

Tab. 2 Langmuir, Freundlich and D–R isotherm parameters.

D–R isotherm constants			Freundlich isotherm constants				Langmuir isotherm constants		
r^2	E (kJ/mol)	k_D (mol^2 k/J^2)	q_m (mg/g)	r^2	n	k_f	r^2	B	q_{max} (mg/g)
0.99	2.19	E^{-7} 1.04-	64.95	0.88	3.44	12.31	0.973	0.06	64.56

2.2.2 Freundlich isotherm

Freundlich isotherm is used for modeling the adsorption on heterogeneous surfaces **(Freundlich, 1906).** This isotherm can be explained by the following equation:

$$q_e = k_f \, c_e^{1/n} \qquad (4)$$

Where, k_f is the Freundlich constant (mg/g) and $\frac{1}{n}$ is the adsorption intensity:

The linear form of the Eq. (4) can be written as:

$$Log \, q_e = Log k_f + \frac{1}{n} Log \, c_e \qquad (5)$$

Fig. 6 shows the dependence of $log q_e$ from $log c_e$ for the natural clay. It is seen that the Freundlich isotherm curves are linear in Cu adsorption. The Freundlich constant k_f and adsorption intensity $\frac{1}{n}$ for Cu are calculated from the slopes of these curves (Tab. 2).
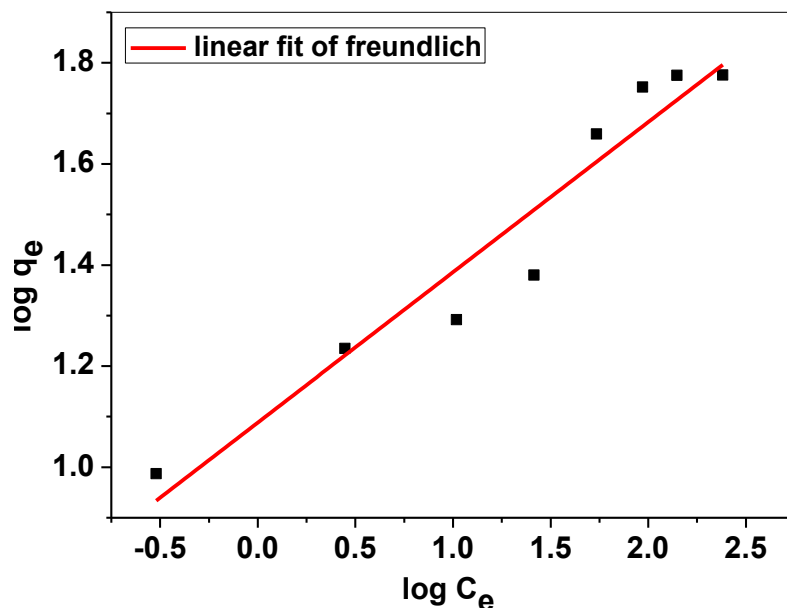
Fig. 6 *Freundlich isotherms for the natural clay.*

2.2.3 Dubinin–Radushkevich (D–R) isotherm

Langmuir and Freundlich isotherms are insufficient to explain the physical and chemical characteristics of adsorption (**Ngah & Fatinathan, 2010**). D–R isotherm is commonly used to describe the sorption isotherms of single solute systems.

The D–R isotherm is expressed as:

$$\ln q_e = \ln q_m - k_D \varepsilon^2 \qquad (6)$$

Where, q_e is the heavy metal amount (mg/g) that is removed per unit clay mass, q_m is the D–R adsorption capacity (mg/g), k_D is the constant related with adsorption energy (mol^{2}k/J^2), and ε is the Polanyi potential.

According to the Eq. (6), the Polanyi potential (ε) can be given as:

$$\varepsilon = RT \ln \left(1 + \frac{1}{c_e}\right) \qquad (7)$$

Where, R is the gas constant (kJK−1 mol−1) and T is the temperature (K).

The main energy of adsorption (E) is calculated by using the following formula:

$$E = \frac{1}{\sqrt{-2k_D}} \qquad (8)$$

Where, E gives information about the physical and chemical features of adsorption.

The D–R isotherm is applied to the data obtained from the studies. As it is seen in (Fig.7), the D–R plot yields a straight line. In the D–R isotherm, adsorption capacities q_m, adsorption energy constants k_D and the main adsorption energies E are calculated for copper removal in (Tab. 2).
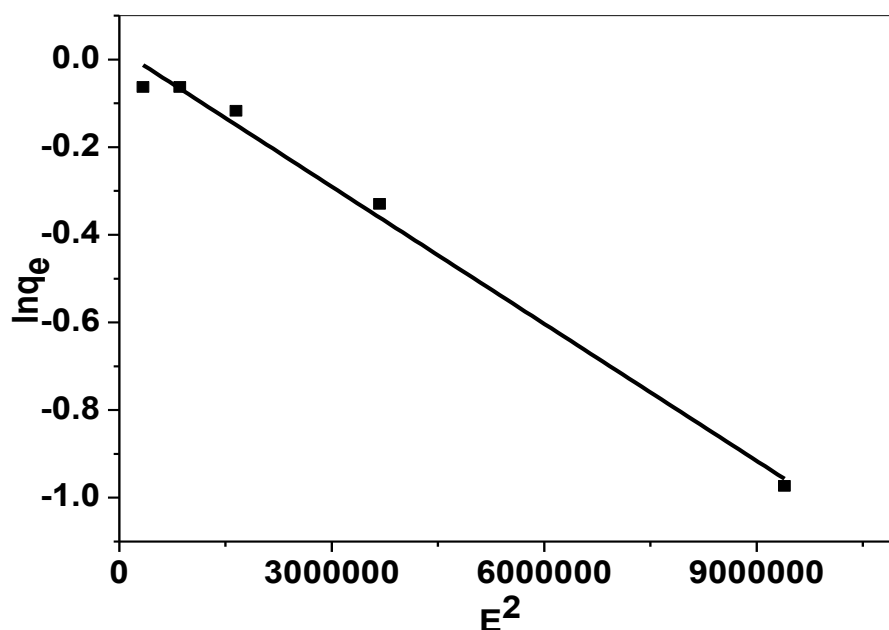
Fig. 7 *D-R isotherms for the natural clay.*

The magnitudes of E for Cu adsorption are 2.19 and 3.19 kJ/mol, respectively. These low values of adsorption energy show that the adsorption has a physical nature.

2.3 Kinetics of adsorption

Adsorption kinetics are used in order to explain the adsorption mechanism and adsorption characteristics.

2.3.1 Pseudo-first-order reaction kinetic

In order to investigate the mechanism of adsorption kinetics, two different kinetic models were tested to interpret data obtained from batch experiments. The pseudo-first-order rate equation of **(Lagergreen, 1898)** is expressed as follows **(Ren et al., 2008)**:

$$Log(q_e - q_t) = Log\, q_e - \frac{k_1}{2.303}t \qquad (9)$$

Where, k_1 the adsorption rate is constant for the first order adsorption, q_t is the amount of heavy metal adsorbed at time t (mg/g) and q_e is the amount of heavy metal adsorbed at saturation (mg/g).

In the study, the initial Cu concentrations were determined as 50, 100, 200 mg/L. The dependences of these concentrations against time are shown in Fig. 8. In order to calculate the adsorption rate constants of Cu, the first order reaction kinetic was applied. For natural clay, it is seen that the curves in the plots of $log(q_e - q_t)$ against time, are linear. Rate constants k_1 were calculated from the slopes of the curves (Tab 3).
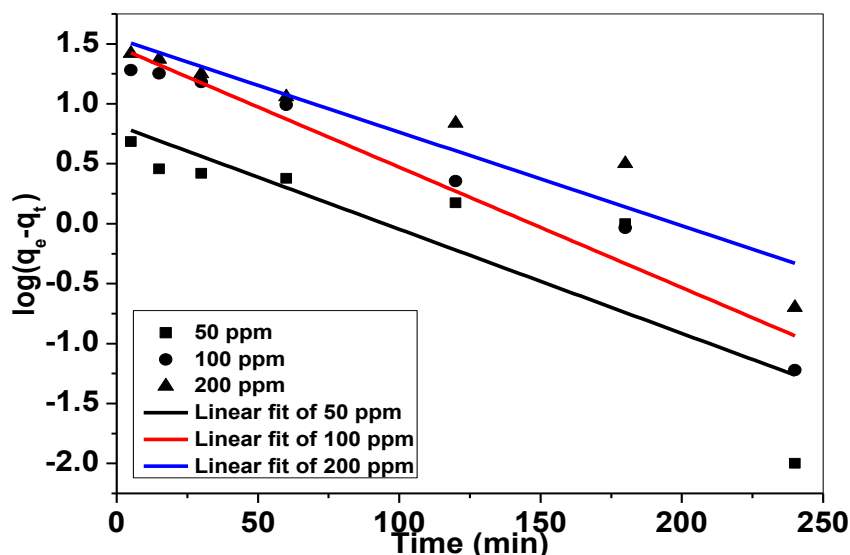
Fig. 8 Pseudo-first order reaction kinetics for the adsorption of copper on natural clay.

Tab. 3 Kinetic parameters for the adsorption of Cu(II) on the natural clay.

Sample	Conc	Pseudo-first-order model			q_e(exp)	Pseudo-second-order model		
		k_1 (h⁻¹)	q_e (mg/g)	r^2	(mg/g)	k_2 (g/mg h)	q_e (mg/g)	r^2
Natural clay	50	0.002	6.65	0.68	22.98	0.213	23.14	0.999
	100	0.23	29.89	0.95	45.04	0.081	46.97	0.998
	200	0.018	35.14	0.88	59.44	0.079	61.5	0.997

2.3.2 Pseudo-second-order reaction kinetic

Adsorption data was also evaluated according to the Pseudo-second-order reaction kinetic proposed by (**Ho & McKay, 1998**):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{10}$$

Where, k_2 is the second order reaction constant. If Eq. (10) is integrated, the following expression is obtained:

$$\frac{1}{q_e - q_t} = k_2 t + c_2 \tag{11}$$

In Eq. (11), c_2 is the integration constant of the second order reaction kinetic. With an algorithmic arrangement, the following statement is formed:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e} t \tag{12}$$

Pseudo-second-order kinetic was also applied for the experimental data of each natural clay. The curves in the plot of $\frac{t}{q_t}$ against t are linear and k_2 rate constants can be calculated from the slope of these curves (Fig. 9).
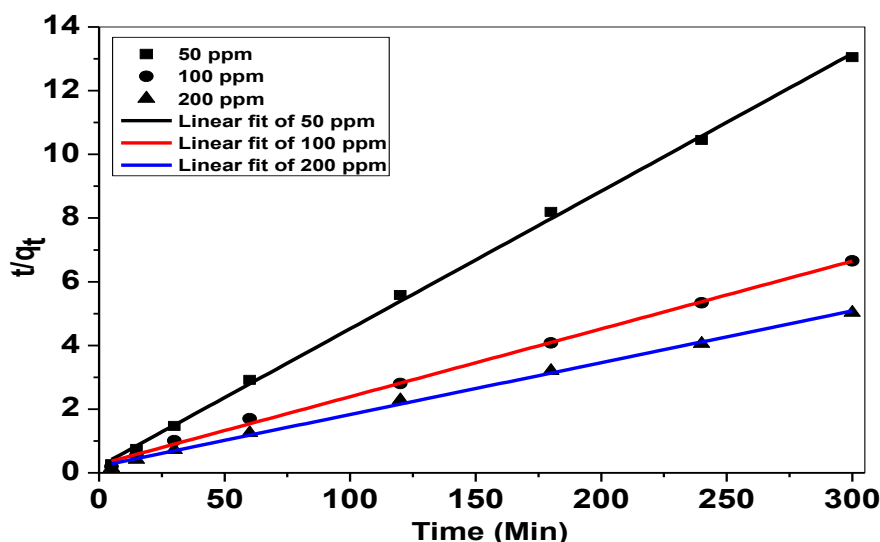
Fig. 9 *Pseudo-second order reaction kinetics for the adsorption of copper on natural clay.*

The values of $q_{e\ calculated}$ are found from the intersection points of the first and second degree reaction kinetic curves. (Tab. 3) presents all of the data.

As the difference between $q_{e\ calculated}$ and $q_{e\ experimental}$ values is considered, it is seen that the Cu removal with natural clay is well followed and described by the second order reaction kinetic. Moreover, all the correlation coefficients of second order reaction kinetic are higher than that of the first order reaction kinetic. So, the results suggested that the pseudo-second-order adsorption mechanism was predominant for this adsorbent system.

3. Discussion and Conclusions

In this work, removal of Cu is investigated using natural clay. pH is a significant factor in adsorption processes since it causes electrostatic changes in the solutions. Hydrogen ions themselves are strongly competing with adsorbates. At the end of experiments carried out at 25 $^{\circ}$C and 200 rpm, optimum pH value for Cu^{2+} removal is determined as 6.

The empirical values are evaluated according to the Langmuir, Freundlich and D–R isotherms that are generally used to describe the adsorption processes. It is stated that all of isotherm models fit very well. By using the Langmuir isotherm, the adsorption capacities for Cu is found as 64.56 mg/g. In the Freundlich isotherm calculated adsorption intensities for copper is 3.44. The correlation coefficients for copper is 0.99. Moreover, in the D–R isotherm, adsorption energies are calculated to state the physical and chemical characteristics of adsorption. The magnitudes of E for copper adsorption is 2.19 kJ/mol, respectively. These low values of adsorption energy show that the adsorption has a physical nature.

Cu adsorption from aqueous solutions using natural clay is well described with the second order reaction kinetic. In the second order reaction kinetic, q_e, calculated and q_e, experimental values are quite close to each other whereas in the first order kinetic the difference between these values are greater. Furthermore, the correlation coefficients are higher in the second order reaction kinetic.

As a result of this study, it may be concluded that natural clay may be used for elimination of heavy metal pollution from wastewater since it is a low-cost, abundant and locally available adsorbent.

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