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Evaluation of copper removal efficiency using water treatment sludge

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Abstract

Large quantities of sludge are produced during water treatment processes. Recently, sludge has been treated as waste and disposed of in landfills, which increases the environmental burdens and the operational cost. Therefore, sludge reuse has become a significant environmental issue. In this study, adsorption of copper ions (Cu^{2+}) onto calcined sludge was investigated under various operational conditions (with varying temperature, Cu^{2+} initial concentration, pH, and sludge dosage). The prepared sludge material was characterized with transmission electron microscopy (TEM), X-ray diffraction (XRD), dynamic light scattering (DLS), and Brunauer-Emmett-Teller (BET) surface area. The sorption capacity of sludge was directly proportional to the initial Cu^{2+} concentration and inversely proportional to the sludge dosage. The optimum operational pH and solution temperature were 6.6 and 80°C, respectively. The experimental results followed a Langmuir isotherm and pseudo-first-order adsorption kinetics. Thermodynamic parameters such as activation energy, change in free energy, enthalpy, and entropy were calculated. Thermodynamic analyses indicated that the sorption of copper ions onto the calcined sludge was driven by a physical adsorption process. The prepared sludge was proven to be an excellent adsorbent material for the removal of Cu^{2+} from an aqueous solution under optimum conditions.

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Keywords: Copper removal; Adsorption; Sludge; Water treatment plant; Operational conditions

1. Introduction

Global demand for drinking water has been increasing exponentially with the world's population, which is growing by 80 million people on average each year (Dassanayake et al., 2015). The treated water required per year is increasing as well, by 64 billion cubic meters annually (Gerbens-Leenes et al., 2009). Coagulation and flocculation using aluminum and iron salts as coagulants for the removal of colloidal impurities from raw water are the main pre-treatment processes employed for water purification. Large quantities of water treatment sludge and residuals are produced as byproducts of those treatment processes (Abhilash and Mansoor, 2015; Razali et al., 2007). Water treatment sludge has a high concentration of organic matter, inorganic salts, and various

oxides (Xu et al., 2016; Zhou et al., 2012). Traditionally, the final destination of water treatment sludge was the nearest stream to the water treatment plant, which caused many environmental problems (Rodrigues and Holanda, 2015). Recently, legislation has classified water treatment sludge as waste that should be chemically conditioned and mechanically dewatered before it is disposed of in landfills (Razali et al., 2007). Water treatment plant operational cost is affected by the expenses of sludge disposal (Evuti and Lawal, 2011; Xu et al., 2009). Therefore, sludge reuse stands as an important and urgent current environmental issue.

On the other hand, heavy metal ions (such as cadmium, chromium, cobalt, copper, nickel, and mercury) have toxicological properties and potential impacts on human health and the environment (Fu and Wang, 2011). These ions are non-degradable and highly harmful even at very low concentrations (Alkorta et al., 2004). Copper spreads in the environment through natural phenomena and industry. Various methods have been used to remove heavy metals from wastewater,

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including reduction and precipitation (Esalah et al., 2000), coagulation and flotation (Zouboulis and Matis, 1997), ion exchange, membrane technologies, and electrolysis (Canet et al., 2002). Those conventional metal removal techniques have some major disadvantages, such as high operational cost, incomplete removal (especially when metal concentration is higher than 100 mg/L), and generation of a large quantity of toxic residuals (Alfassi and Wai, 1992; Miretzky et al., 2006). In contrast, adsorption is an effective technique for the removal of non-biodegradable pollutants from water (Nhapi et al., 2011; Saka et al., 2012). Researchers have used many adsorbent materials for the removal of copper ions from wastewater, including binary compounds, hazelnut husks, maghnite clay, and rubber wood saw dust (Kongsuwan et al., 2009; Imamoglu and Tekir, 2008; Zenasni et al., 2012; Kalavathy et al., 2005). Kongsuwan et al. (2009) explored the use of activated carbon (AC) from eucalyptus bark in the binary component sorption of copper ions. The maximum sorption capacity for Cu^{2+} was 28.35 mg/g. Zenasni et al. (2012) achieved a removal efficiency of 94% after 120 min of contact time. The maximum sorption capacity for Cu^{2+} was 5.72 mg/g using rubber wood saw sand and an adsorbent dosage of 5 g/L (Kalavathy et al., 2005).

Water treatment sludge can be used as adsorbent material for heavy metal removal due to the presence of various oxides in its components and because of its large surface area. Although studying the effect of operational conditions on the sorption capacity of sludge to adsorb heavy metals and understanding the sorption kinetics and thermodynamics of sludge are required to improve the sludge sorption performance, only a few studies have addressed these issues (Lee et al., 2006).

This study aimed to investigate an environmentally friendly and practical method for the removal of copper ions from an aqueous solution using calcined sludge as an adsorbent material. The effects of operational conditions (temperature, initial Cu^{2+} concentration, pH, and sludge dosage) on the adsorption removal efficiency and sorption capacity of the calcined sludge were examined. Sorption isotherms and kinetics were investigated. The thermodynamic parameters were also analyzed and evaluated for the adsorbent material.

2. Materials and methodology

2.1. Calcined sludge preparation

A sludge sample was taken from the drying beds of a water treatment plant in Zagazig City, Egypt. The water treatment sludge was first dried at 100°C for 24 h, and then aerobically calcined at 500°C for 4 h. The calcined sample was sieved through 200 meshes, to increase the area of contact with the adsorbate during the reaction. The calcined powder was washed before usage, to remove any impurities from the adsorbent surface that might have influenced the sorption reaction. Then, it was placed in the oven and dried at 100°C before usage.

2.2. Sludge characteristics

Thermal gravimetric analysis (TGA) was conducted using SETARAM Labsys TGDSC16 equipment at a temperature ranging from 16°C to 1000°C to identify the thermal stability of the calcined sludge. X-ray diffraction (XRD) analysis was carried out using a Shimadzu XD-1 diffractometer. High-resolution transmission electron microscopy (HRTEM) and energy-dispersive X-ray (EDX) analysis were carried out using a JEOL 2100F transmission electron microscope at an accelerating voltage of 200 KV. The textural properties were measured from the N_2 adsorption-desorption isotherms at the temperature of -196°C using a NOVA2000 gas sorption analyzer system (Quanta Chrome Corporation). The BET surface area (SBET) was calculated using the five-point Brunauer-Emmett-Teller (BET) theory. Dynamic light scattering (DLS) verified the particle size distribution of samples using a Zetasizer Nano ZS90 (Malvern Instruments) operating at 90 nm and 600 nm.

2.3. Adsorption experiments

All chemicals utilized in this study were of analytical grade. A standard solution (1000 mg/L) of copper was prepared using copper chloride (CuCl_2). The solution was diluted to the required concentrations before being utilized. Batch adsorption experiments were performed by shaking the desired amount of the sludge adsorbent with 10 mL of copper chloride solution. To adjust the solution pH, a solution of HCl or NaOH with a concentration of 0.1 mol/L was used. The solutions for each experiment were shaken at 400 rpm using a Velp Scientific shaker in a 50-mL capped flask.

A series of laboratory experiments was conducted to investigate the effects of operational conditions (temperature, initial Cu^{2+} concentration, pH, and sludge dosage) on the removal efficiency and sludge sorption capacity. The pH value of the solution was gradually increased from 2.8 to 11. The solution initial concentration was gradually increased from 50 to 1000 mg/L. The adsorbent dosage was gradually changed from 0.05 to 0.25 g. The solution temperature was gradually increased from 16°C to 100°C. Before analysis, the adsorption solution was filtered through Whatman 42 filter paper. The copper concentration was measured with a spectrophotometric technique (unico/4802 UV/Vis double) at a wavelength of 620 nm using a reagent of ammonia solution. The results are expressed in terms of removal efficiency E (%) and adsorption capacity A (mg/g), according to the following relationships:

$$E = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$A = \frac{C_0 - C_e}{m} V \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations of copper ions in the solution (mg/L), respectively, m is the mass of adsorbent (g), and V is the volume of solution (L).

Sorption isotherms and kinetic models for the calcined sludge were investigated. Thermodynamic parameters, such as the changes of enthalpy (ΔH), entropy (ΔS), and adsorption free energy (ΔG) were identified for the adsorbent material. Each experiment was carried out two times to ensure the reliability of the obtained results.

3. Results and discussion

3.1. Sludge characteristic analysis

Water contents of the dry and wet samples at 100°C were 0 and 21.7%, respectively. The specific surface area of the dried (100°C) and calcined (500°C) samples were 19 and 35 m²/g, respectively. The pore volumes for the dried and calcined sludge were 0.03955 and 0.07927 cm³/g, respectively. The obtained results confirmed that the calcined sludge had a larger specific surface area and pore volume than the dried sample, which enhanced the adsorption capacity of the calcined sludge. The TEM analysis illustrates the morphology of the calcined sludge material. Fig. 1 confirms that the prepared sludge had a layered structure.

3.1.1. Thermal analysis

Fig. 2 shows the graphical profile of TGA of a dried sludge sample using a heating rate of 20°C per minute. When the sample temperature was raised from 20°C to 40°C, most of the moisture was forced out. This indicates the presence of free or unbound water. A small loss was noticed with the rise of the temperature from 40°C to 110°C, which may have been due to the strong physical bond between water and sludge. The water contiguous to aluminum hydroxide was driven out at a temperature between 200°C and 400°C. Carbon dioxide was evolved at temperatures greater than 650°C. According to the graph, the best heating temperature should be between 450°C and 500°C. Using a temperature higher than 500°C is not recommended, based on the demonstrated change in the sludge characteristics.

3.1.2. Energy-dispersive X-ray and X-ray diffraction analysis

EDX elemental mapping for the water treatment sludge identified the presence of silicon oxide (SiO₂), aluminum oxide (Al₂O₃), and iron oxide (Fe₂O₃). Fig. 3 shows the XRD pattern of calcined sludge, where 2θ is the angle between the beam and detector. The peaks of 20.96°, 28.10°, and 50.20°

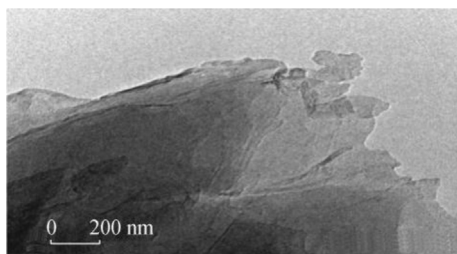


Fig. 1. TEM image of calcined sludge.

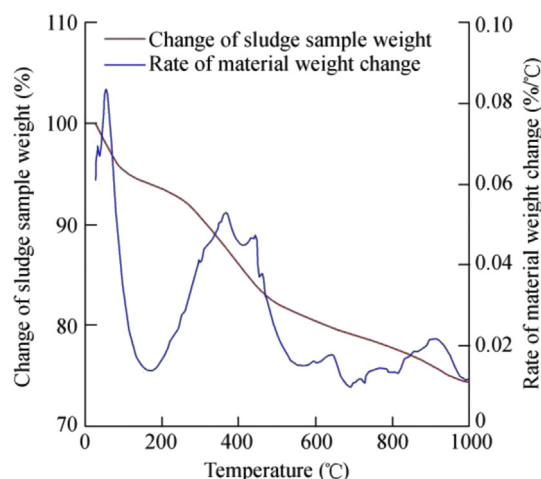


Fig. 2. TGA profile of dried sludge sample.

indicate the presence of silica. The reflections at 26.73° and 36.63° may be due to the presence of potassium aluminum sulfate. The peaks located at 26.73°, 39.53°, and 68.28° are related to Al₂O₃. Also, Fe₂O₃ was detected at a reflection of 42.33°. The presence of those elements was evidenced by EDX data.

3.1.3. Particle size distribution

The particle size distribution of the calcined sludge is illustrated in Fig. 4. The curve shows the bimodal particle size distribution in the ranges of 68–220 nm and 342–1106 nm. The portion of large particles is around 105 nm. The distribution of particles of large size may be attributed to the floc formation.

3.2. Adsorption results

3.2.1. Effects of initial Cu²⁺ concentration and contact time

Sludge sorption capacity and removal efficiency were investigated at various initial copper concentrations from 50 to 1000 mg/L at a pH value of 4.8 and a temperature of 20°C using 0.25 g of calcined sludge sample. Figs. 5 and 6 show the effects of both C_0 and solution/adsorbent contact time (t_c) on the adsorption capacity of the calcined sludge and the removal efficiency, respectively. It is clear that Cu²⁺ concentrations are directly proportional to the adsorption capacity of sludge adsorbent. This may be due to the enhancement of metal ion

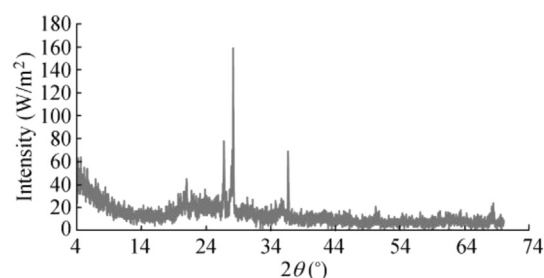


Fig. 3. XRD of calcined sludge sample.

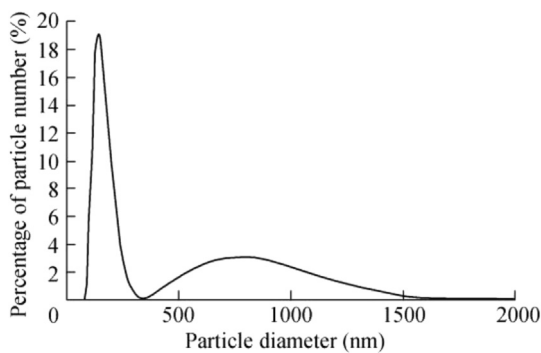


Fig. 4. Particle size distribution of calcined sample.

mass transfer, as the initial concentrations are directly proportional to the driving force (Wan et al., 2013). The adsorption capacity increased from 1.90 to 35.5 mg/g with the increase of the concentration from 50 to 1000 mg/L. This study achieved higher adsorption capacity than previous studies using rubber wood saw dust, hazelnut husk, and binary compounds as adsorbent materials (Kongsuwan et al., 2009; Imamoglu and Tekir, 2008; Kalavathy et al., 2005). In this study, 100% adsorption capacity was reached at less than 80 min at 25°C, while the adsorption of Cu^{2+} on the maghnite clay was only 94% at 120 min (Zenasni et al., 2012). It was noted that lower concentrations require less contact time than higher ones to reach the saturation stage.

Moreover, Fig. 6 demonstrates that the adsorption rates increased sharply at the beginning and then stabilized, forming a plateau. This indicates that the equilibrium was attained gradually. Cu^{2+} removal efficiency was inversely related to solution concentration. At C_0 higher than 500 mg/L, the number of shared electrons will increase, which leads to strong metal-adsorbent interactions (Masel, 1996).

The removal efficiency decreased from 100% to 88.6% with the increase of the concentration from 50 to 1000 mg/L. As shown in Fig. 6, the calcined sludge sample can remove more than 80% of Cu^{2+} at a C_0 value equal to 1000 mg/L. Moreover, when adsorbate concentrations decreased, the adsorption capacity of the adsorbent attained saturation

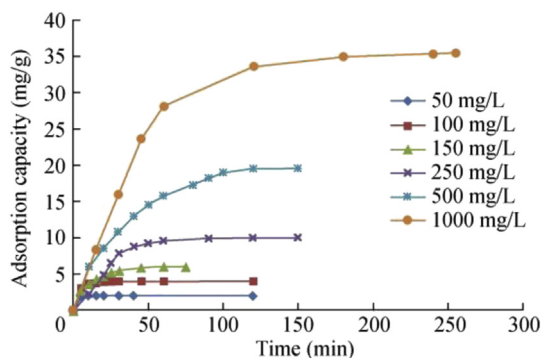
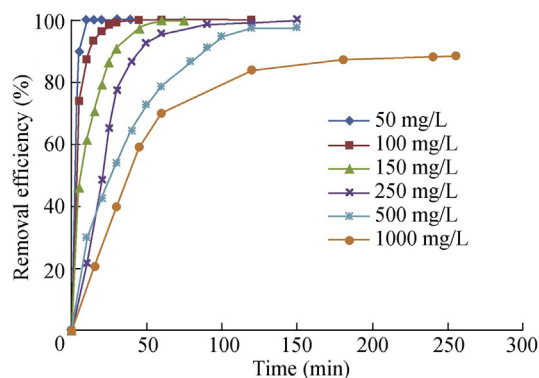


Fig. 5. Effects of initial concentration and contact time on adsorption capacity of calcined sludge sample (with pH value of 4.8, temperature of 20°C, and adsorbent weight of 0.25 g).

Fig. 6. Cu^{2+} removal efficiency at different initial concentrations and contact times.

instantaneously, and the removal efficiency of Cu^{2+} increased. This may be related to the fact that the number of adsorption sites available are insufficient, and hence a greater amount of sludge adsorbent is needed to achieve higher removal efficiency.

3.2.2. Effect of Cu^{2+} solution pH

The pH value of the solution affects the dissociation degree of the adsorbent functional groups and the solubility of the metal ions. The pH value was increased from 2.8 to 11.0 using 0.25 g of adsorbent and an initial concentration of 1000 mg/L at a temperature of 20°C. Fig. 7 shows the influence of solution pH on removal efficiency and adsorption capacity of the calcined sludge. It was found that, as the pH value increased, the adsorption capacity increased at a pH value of 6.6, then gradually decreased. This may be related to the fact that, at pH values less than 6.6, the metal ions are totally dissolvable, while at a higher pH value precipitation takes place. Moreover, in acidic media, there is a competition between H^+ ions and metal ions to bind with the sludge basic functional groups (Veil and Alyüz, 2007; Wan et al., 2013). According to the results, in order to reach the highest removal efficiency, the recommended pH value is in the range of 5–10.

3.2.3. Effect of sludge-adsorbent dosage

The experiment was conducted using an initial concentration of 1000 mg/L at a pH value of 4.8 and a temperature of 20°C. The adsorbent weight was increased from 0.05 to 0.25 g. Fig. 8 shows the influence of sludge-adsorbent dosage on copper ion removal efficiency and adsorption capacity of the calcined sludge. It was found that, as the adsorbent weight increased, the removal efficiency increased. This indicates that as the adsorbent weight increases, the available adsorption sites for Cu^{2+} increase, helping to achieve higher removal efficiency (Mobasherpour et al., 2014). Conversely, the adsorption capacity decreased from 100 to 30 mg/g with an adsorbent weight increasing from 0.05 to 0.25 g. This leads to the conclusion that the percentage of adsorption area occupied

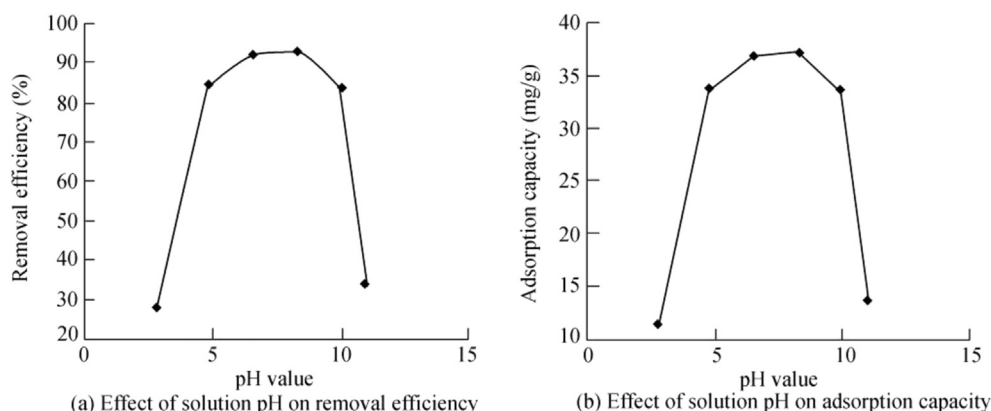


Fig. 7. Effects of solution pH on removal efficiency and adsorption capacity of calcined sludge (with adsorbent weight of 0.25 g, temperature of 20°C, and contact time of 120 min).

by adsorbate ions decreases as the adsorbent weight increases, using the same initial concentration of ions.

3.2.4. Effect of solution temperature

To study the effect of solution temperature on adsorption of Cu^{2+} by calcined sludge, the solution temperature was raised from 16°C to 100°C. Fig. 9 shows the effects of temperature on both removal efficiency and adsorption capacity of sludge adsorbent at a contact time of 120 min, a pH value equal to 4.8 using an adsorbent weight of 0.25 g and an initial concentration of 1000 mg/L. The removal efficiency increased from 84% at 20°C to 90% at 80°C, then decreased. This indicates that the adsorption of Cu^{2+} on calcined sludge sample is favorable at a high solution temperature. This may be due to the increase of copper ion mobility at high temperature and the increase of molecule number in order to obtain sufficient energy to undergo an interaction with active sites at the surface (Todorciuc et al., 2015).

3.2.5. Thermodynamic analysis

The thermodynamic parameters were determined using the following equations:

$$\Delta G = -RT \ln K_d \quad (3)$$

where R is the universal gas constant equal to 8.314 J/mol, T is the temperature in Kelvin (K), and K_d is the distribution ratio, expressed by

$$K_d = \frac{aV}{bm} \quad (4)$$

where a is the amount of metal in the adsorbent and b is the amount of metal in the solution.

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

In Fig. 10, the enthalpy is the intercept of the linear plots of adsorption free energy versus temperature, the entropy is the slope, and R^2 is the coefficient of determination. Fig. 11 shows the increase of K_d with gradually increasing temperature, which demonstrates the endothermic nature of adsorption. The negative ΔG values at different temperatures demonstrate the spontaneous nature of the adsorption process. Additionally, the positive ΔH value demonstrates that the adsorption was endothermic. The change in free energy in the range of 0–20 kJ/mol indicates a physical adsorption reaction, while a

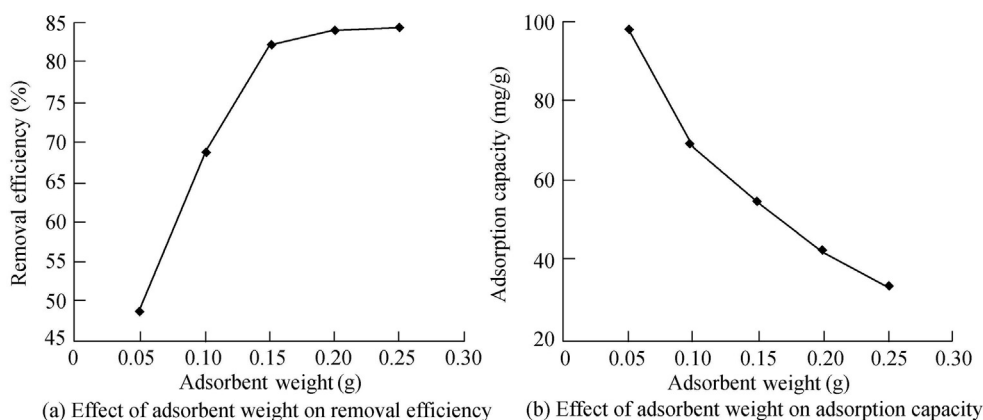


Fig. 8. Effects of adsorbent weight on removal efficiency and adsorption capacity (with initial concentration of 1000 mg/L, pH value of 4.8, temperature of 16°C, and contact time of 120 min).

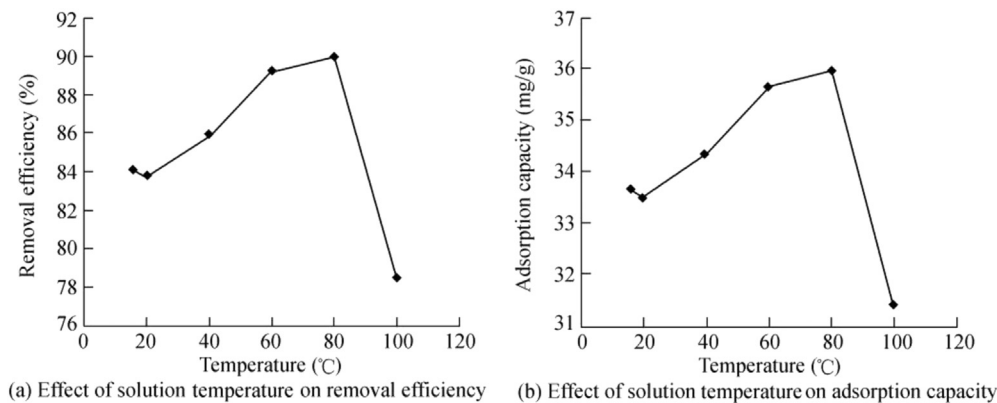


Fig. 9. Effects of solution temperature on removal efficiency and adsorption capacity of calcined sludge (with initial concentration of 1000 mg/L, pH value of 4.8, contact time of 120 min, and adsorbent weight of 0.25 g).

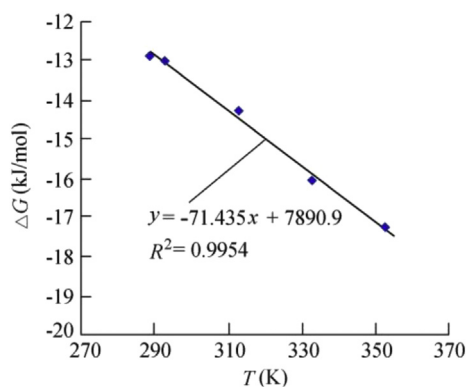


Fig. 10. Adsorption free energy versus temperature.

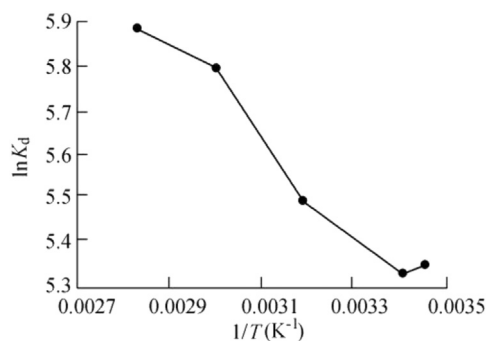


Fig. 11. $\ln K_d$ versus $1/T$.

higher value between 80 and 400 kJ/mol indicates a chemisorption process (Yu et al., 2001). The free energy values obtained ranged from -12.85 to -17.28 kJ/mol at temperature values ranging from 289 to 373 K. These results reveal that the sorption between Cu^{2+} and sludge is mainly physical adsorption. If ΔH is less than 84 kJ/mol, the adsorption process is physical (Faust and Aly, 1987). The obtained ΔH value was 7.89 kJ/mol, which is in the physical adsorption range. It can be concluded that the Cu^{2+} adsorption onto sludge is a physical adsorption process.

3.2.6. Adsorption isotherm

The sorption data were investigated using the Langmuir and Freundlich sorption isotherms (Fig. 12).

The Langmuir and Freundlich isotherms were employed to validate the experimental results for copper chloride adsorption onto calcined sludge. The form of the Langmuir adsorption isotherm can be represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K} + \frac{C_e}{Q_0} \quad (6)$$

where K is the Langmuir constant (L/mg), Q_0 is the maximum adsorption capacity of calcined sludge (mg/g), and q_e is the copper chloride amount that is adsorbed at equilibrium (mg/g). The Langmuir model can describe the experimental data with a value of R^2 equal to 0.993. Based on the data, the adsorption occurs at specific homogeneous sites from the sludge surface and it is monolayer sorption without interaction between adsorbed molecules (i.e., once a metal ion occupies a site, no further adsorption can occur at that site).

The Freundlich model (Eq. (7)) has been used to express the experimental data, providing data about the surface

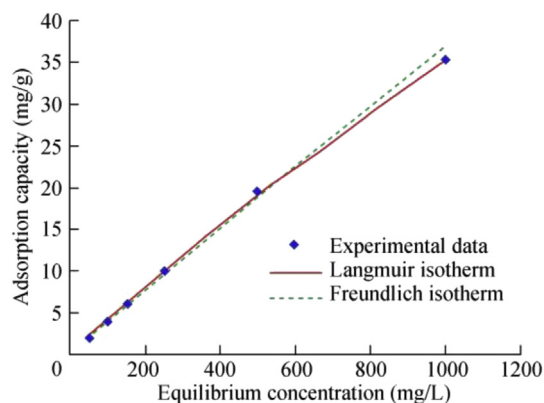


Fig. 12. Langmuir and Freundlich sorption isotherms for adsorption of Cu^{2+} onto calcined sludge.

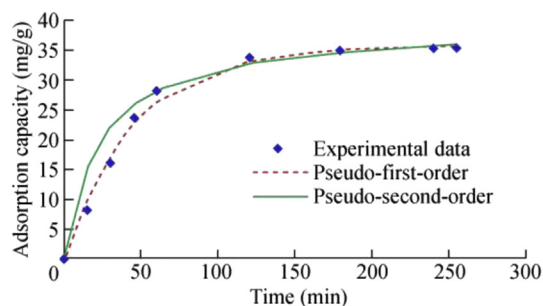


Fig. 13. First- and second-order reversible reaction kinetics plot for adsorption of Cu^{2+} onto calcined sludge.

heterogeneity and the distribution of active sites and their energies.

$$\lg q_e = \lg K_f + \frac{1}{n_f} + \lg C_e \quad (7)$$

where K_f is the Freundlich constant, and n_f is a constant that shows the copper ions' affinity toward the calcined sludge.

The R^2 value was 0.947, which indicates the validation of the model for expressing the experimental data. Furthermore, the constant $1/n_f$, which measures the deviation of the adsorption from linearity, produced a value of n_f equal to 3.748, which indicates a favorable adsorption process. It is clear that the Langmuir isotherm can describe the adsorption data better than the Freundlich isotherm, according to the R^2 value.

3.2.7. Adsorption kinetics

To illustrate the controlling mechanism of the adsorption processes, pseudo-first-order and pseudo-second-order kinetic equations were both used to describe the experimental data. The pseudo-first-order equation is as follows:

$$\lg(q_e - q_t) = \lg q_e - \frac{k_1}{2.303} t \quad (8)$$

where q_t is the amount of adsorbed Cu^{2+} at time t (min), and k_1 is the pseudo-first-order rate constant (min^{-1}).

The pseudo-second-order kinetic model is based on the assumption that chemisorption is the rate-determining step as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (9)$$

where k_2 is the pseudo-second-order rate constant ($\text{g}/(\text{mg} \cdot \text{min})$).

Fig. 13 shows the fitting between the model equations and the experimental data. The pseudo-first-order and pseudo-second-order R^2 were 0.9918 and 0.9674, respectively. It is clear that ion adsorption onto the calcined sludge was represented by both pseudo-first-order and pseudo-second-order models, but the pseudo-first-order model provided a better correlation. This confirms that the adsorption mechanism of Cu^{2+} onto the sludge is a physical adsorption process.

4. Conclusions

The main purpose of this study was the use of a highly efficient and low-cost adsorbent derived from the sludge produced from a drinking water treatment plant as an available material for the removal of copper ions. The adsorbent material was first characterized using various techniques, including XRD, DLS, TEM, and BET surface area. For the adsorption process, the optimum pH, effective concentration, adsorbent dosage, reaction time, and temperature were optimized. It was found that the sorption capacity of calcined sludge was directly related to the copper ion initial concentration and inversely related to adsorbent dosage. The highest removal efficiency and sorption capacity were achieved at a pH value of 6.6 and a solution temperature of 80°C . The experimental results followed the Langmuir model and pseudo-first-order adsorption model. Thermodynamic parameters indicate the endothermic nature and the spontaneous nature of the adsorption process. Thermodynamic analyses prove that the sorption of Cu^{2+} onto the sludge was mainly a physical adsorption process. The calcined sludge was shown to be a proper adsorption material for copper ion removal from an aqueous solution, which will help to reduce the burdens on the environment.

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