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Effecting of Temperature and Particles of Fly Ash on Copper Ion Adsorption From Aqueous Solutions

Salem M. Alburki [1*], Fadela M. Elzalet [1]
[1] Chemical and Petroleum Engineering Department, Faculty of Engineering, El-Mergib University, Al-Khums, Libya

دراسة تأثير درجة الحرارة وجزيئات الرماد المتطاير على امتصاص أيونات النحاس من المحاليل المائية

سالم محمد البركي [1*]، فضيلة محمد الزالط[1]
[1] قسم الهندسة الكيميائية والنفطية، كلية الهندسة، جامعة المرقب، الخمس، ليبيا

*Corresponding author: smalburki@elmergib.edu.ly

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Abstract:
This study examined the impact of fundamental factors that significantly influence the removal of pollutants from aqueous solutions through adsorption processes, particularly heavy metal ions. These ions can build up and remain unresolved, leading to numerous issues. This study utilized fly ash, one of the numerous natural adsorbents, to eliminate copper ions. We studied the impact of fly ash particle size and the temperature's extent on the adsorption process. We also calculated the value of free energy and enthalpy to simulate the nature of adsorption in the presence of a temperature change. The laboratory results indicated that the adsorbent's best size is the smallest size available, which is 0.075 mm, and the best temperature was 60 °C.

Keywords: Adsorption, Fly Ash, Copper ion, Temperature.

الملخص
تبحث هذه الدراسة تأثير العوامل الأساسية التي تؤثر بشكل كبير على إزالة الملوثات من المحاليل المائية من خلال عمليات الامتزاز، خاصة أيونات المعادن الثقيلة. يمكن لهذه الأيونات أن تتراكم وتظل غير محلولة، مما يؤدي إلى العديد من المشاكل. استخدمت هذه الدراسة الرماد المتطاير، وهو واحد من العديد من الممتزات الطبيعية، لإزالة أيونات النحاس. قمنا بدراسة تأثير حجم جزيئات الرماد المتطاير ومدى تأثير درجة الحرارة على عملية الامتزاز. كما قمنا بحساب قيمة الطاقة الحرة والإنثالبي لمحاكاة طبيعة الامتزاز في ظل تغير درجة الحرارة. أشارت النتائج المعملية إلى أن أفضل حجم للممتز هو أصغر حجم متاح، والذي يبلغ 0.075 مم، وأفضل درجة حرارة كانت 60 درجة مئوية.

الكلمات المفتاحية: الامتزاز، الرماد المتطاير، أيون النحاس، درجة الحرارة.

1. Introduction

Water is considered an essential element in all forms of plant and animal life, and water pollution is usually considered more important than soil and air pollution due to the urgent need for water, Because of its special characteristics and qualities, the best dissolving agent available can be suspended or absorbed in a wide range of materials. Two to three billion people worldwide lack basic sanitation, and more than one billion do not have access to safe drinking water. The diseases associated of with polluted water can kill between (3,5) million people every year [1]. The major pollutants in water sources due to water content of heavy metals ions, these heavy metals are sensitive indicators for monitoring changes in the marine environment, the levels of heavy metals in the aquatic environment are seriously increasing because of human industrial activities and creates great global concern [2], [3].

Some of these minerals are essential for the growth, development, and health of living organisms, but the others are non-essential and indestructible, and most of them are classified as toxic species to living organisms, therefore the toxicity of metals depends on concentration levels in the environment, these concentrations increase because the ability of soil to retain heavy metals, that seep into groundwater and soil solutions [4],[5]. Consequently, these toxic metals can accumulate in living tissues and concentrate throughout the food chain. the toxic metals are:

1. Cadmium is considered one of the most dangerous pollutants in the modern.
2. Copper is classified as a priority pollutant due to its adverse health effects [6].
3. Zinc and iron are essential elements which generally considered non-toxic at certain levels [7].
4. Lead is not an essential trace element in any organism and has no known biological function that can cause a variety of harmful health effects [8].

The main causes of massive accumulation of heavy metals in water are natural and human, the additional natural sources of heavy metal water pollution include wet and dry deposition of atmospheric salts, water contact with rocks, and the interaction of water with One human cause of polluted water is the sudden rise in urbanization and industrialization [9]. Table 1 shows the sources of heavy metal ions in water used in industrial and chemical processes.

Table (1): Major sources of some heavy metal ions in water [10]

Heavy metal ion	Common source
Copper (Cu)	Fertilizers, tanning, and photovoltaic cells
Zinc (Zn)	Soldering, cosmetics, and pigment
Cadmium (Cd)	Paints, pigments, electroplated parts, synthetic rubber, photoconductors
Mercury (Hg)	Combustion of coal, municipal solid waste incineration
Chromium (Cr)	Leather industry, chrome plating industries, and tanning
Arsenic (As)	Pesticides, fertilizers, and oxidation of pyrite (FeS)

Removal of copper ions has become increasingly important from an economic and environmental standpoint due to their serious risks to humans, animals and plants. Copper (II) contamination in the environment usually causes significant health consequences because it accumulates in living tissues throughout food. Chain as a non-degradable contaminant [8,11]. Removal of copper ions from aquatic systems is extremely important, this process is called (Adsorption), this process is used the ion-metal interface by fly ash is often used as a very effective method to expel unwanted metal from the aqueous phase [12], [13].

Adsorption works on the principle of adhesion, in the case of water treatment organic contaminants are attracted to the adsorbent, which adhere to its surface through a combination of complex physical forces and chemical action. For adsorption to be effective, the adsorbent must provide a very large surface area to which contaminating chemicals can adhere [14],[15],[16].
In [17]. This paper provides a comprehensive overview of the potential uses of fly ash as an adsorbent for various organic pollutants, including dyes, phenols, and pesticides. The author discusses the advantages of using fly ash, such as its abundance and low cost. The paper also covers the modification techniques used to enhance the adsorption capacity of fly ash, such as thermal and chemical treatments.

This research [18] evaluates the use of chemically modified fly ash for the adsorption of dyes such as methylene blue and methyl orange from aqueous solutions. The fly ash was modified using acids and alkalis to enhance its adsorption properties. The study found that modified fly ash exhibited significantly higher adsorption capacities for both dyes compared to unmodified fly ash. Adsorption isotherms and kinetics were studied, and the results showed that the adsorption data fit well with the Langmuir isotherm model and pseudo-second-order kinetics, indicating efficient and fast adsorption processes.

According to [19], the article studied adsorption of phenolic compounds, on fly ash. study found that fly ash has a considerable capacity to adsorb these compounds from aqueous solutions. The article concluded that the adsorption capacity of fly ash for phenolic compounds is comparable to other low-cost adsorbents, making it a viable option for wastewater treatment. In [20], this study explores how modifying fly ash impacts its ability to adsorb heavy metals such as Pb (II), Cd(II), and Zn(II). The fly ash was treated with acids to enhance its surface area and active sites. The study found that acidtreated fly ash had a significantly higher adsorption capacity compared to untreated fly ash. The adsorption process was influenced by environmental conditions such as pH and temperature, with optimal adsorption occurring at acidic pH levels. The adsorption mechanisms were found to involve ion exchange and complexation with the functional groups on the fly ash surface.

2. Materials and Methods

2.1 Preparation of fly Ash

Fly ash is a byproduct of burning pulverized coal in electric power plants and cement factories, that consist of fine particles that are ejected from the combustion chamber with the flue gases and are collected by electrostatic precipitators or other particulate filtration equipment before the flue gases reach the chimneys of coal-fired and other power plants. Fly ash is primarily composed of silica (SiO2), alumina (Al2O3), iron oxides (Fe2O3), and calcium oxide (CaO). It may also contain trace amounts of other elements such as magnesium, sulfur, sodium, potassium, and carbon [21].

Table (2): Chemical Composition of fly ash.

Chemical Component	Chemical Formula	Approximate Percentage (%)
Silicon Dioxide	SiO_2	20% - 60%
Aluminum Oxide	Al_2O_3	10% - 30%
Iron Oxide	Fe_2O_3	5% - 10%
Calcium Oxide	CaO	1% - 40%
Magnesium Oxide	MgO	1% - 5%
Sulfur Trioxide	SO_3	<5%
Sodium Oxide	Na_2O	<5%
Potassium Oxide	K_2O	<5%
Carbon Content	C	<5%

In this work, the chemical composition of the fly as are used, that has been analyzed, and the XRD results show that the fly ash contains SiO2 and Al2O3 in different proportions, as well as an amount of CaO. Therefore, all fly ash can be classified as high calcium.

Table (3): Chemical Composition of Fly Ash.

Constituent	AL2O3	CaO	Cl	Fe2O3	K2O
wt. (%)	4.6877	52.7283	0.0103	3.0613	1.719
Constituent	MgO	Na2O	SiO2	SO3	Others
wt. (%)	1.1993	0.3539	17.126	0.0997	19.0145

The Particles of fly ash which were separated in various sizes and ranged between (0.075-0.15-0.3-0.4-0.5) mm, depending on the size of the sieves that employed to separate the particles. All other parameters (concentration = 3000 ppm, pH = 5, temperature = 25 °C, dosage = 3.5 g) remained constant.

Figure (1): Fly Ash.

2.2 Preparation of The Solution

The creation of stock solution needs of Cu2+ ions (3000 mg/L) and the appropriate volumes of CuSO4.5H2O were dissolved in purifying water, after that transferred them in 50 mL volumetric container. The stock solution with distilled water is allowed to the Cu2+ standard solution to have a specified concentration range.

Figure (2): Preparation of solution

2.3 Spectrophotometer

The spectrometer used to analyze copper levels in various samples, both prior to and following treatment, was manufactured by Labmod, Inc., U.S.A. This instrument played a crucial role in determining the concentration of copper ions in the samples. Figure 3 illustrates the spectrophotometer used in the experiment.

Figure (3): Spectrophotometer.

2.4 Laboratory Water Bath

The laboratory water bath is employed to heat samples to specific temperatures. By submerging the samples in water, this apparatus ensures that they reach the required temperature, which is crucial for calculating the final concentrations, absorption volume, and removal percentage. Figure 4 illustrates the laboratory water bath used in these experiments.

Figure (4): Laboratory water bath.

3. Adsorption Experiments

The study of copper adsorption of this process was carried out in multi trails. A series of flasks content (50 ml of 3000 mg/L Cu (II)) at an initial temperature of 25 °C were shaken with different amounts of fly ash starting (1 g), the solutions were filtered using filter paper and the concentration of ions of Cu (II) was estimated by spectrophotometry. In order to proof the effectiveness, the particle size and temperature on the adsorption of copper (II) ions after a time, filtration takes place of these samples with concentrations of ions copper (II). All tests were carried out in duplicate. The data were thrown when the exceeding of errors to 5%, and the trails was repeated until the error decreasing the value of error. The removal value of the copper ion was calculated through the relationship as presented in Eq. (1) [22], [23].

$$R = \frac{(C_\mathrm{i} - C_f)}{C_\mathrm{i}} * 100 \qquad (1)$$

Where:

C_i : Initial copper ion concentration of Cu II mg/L
C_f: Final concentration of Cu II mg/L

The amount of element ions adsorbed on the surface of the adsorbent is also calculated through the relationship as shown in Eq. (2) [23].

$$Q_e = \frac{(C_\mathrm{i} - C_e)\mathrm{v}}{m} \qquad (2)$$

Where:

Q_e: Adsorption capacity at equilibrium (mg/L).
C_e: The final concentration of the element ion after the adsorption process and at equilibrium (mg/L).
v: Volume of the prepared aqueous solution
m: is the mass of the adsorbent in grams.

4. Results and Discussion

Data includes variations in parameters affecting the removal of Cu (II) from synthetic solutions, such as temperature, and particle size of the adsorbent, the equilibrium equation and thermodynamic studies are presented. This is followed by a presentation of the results of kinetic studies, which provide a description of the adsorption mechanism that occurs through this process.

4.1 Selection of The Wave Length

Prior to initiating the copper concentration measurement tests, the ideal wavelength was investigated. Figure 5 illustrates the relationship between wavelength and absorptivity. The picture below illustrates how absorption rises with reaching of wavelength, which its maximum at 800 nm. Then, the wavelength increases, the absorption begins to diminish. As a result, copper in samples is quantitatively analyzed using this wavelength.

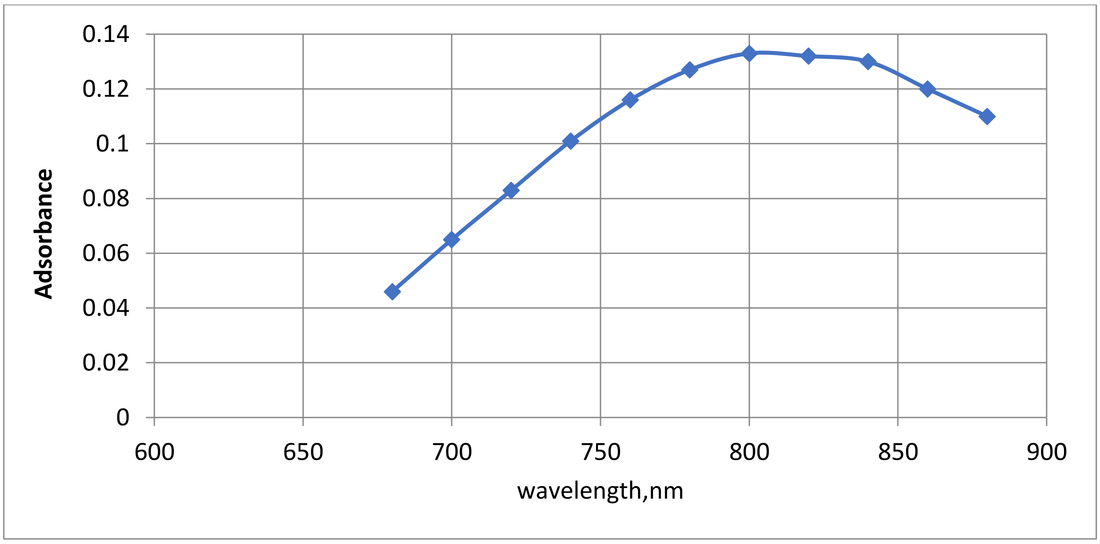

Figure (5): Maximum absorbent of copper (II) solution

4.2 Calibration Curve

Calibration curves performed before operating the UV-9200 UV-Visible Spectrophotometer to measure copper ions in solution to obtain accurate results. Figure 6 presents Calibration curve of cu(ii) solution.

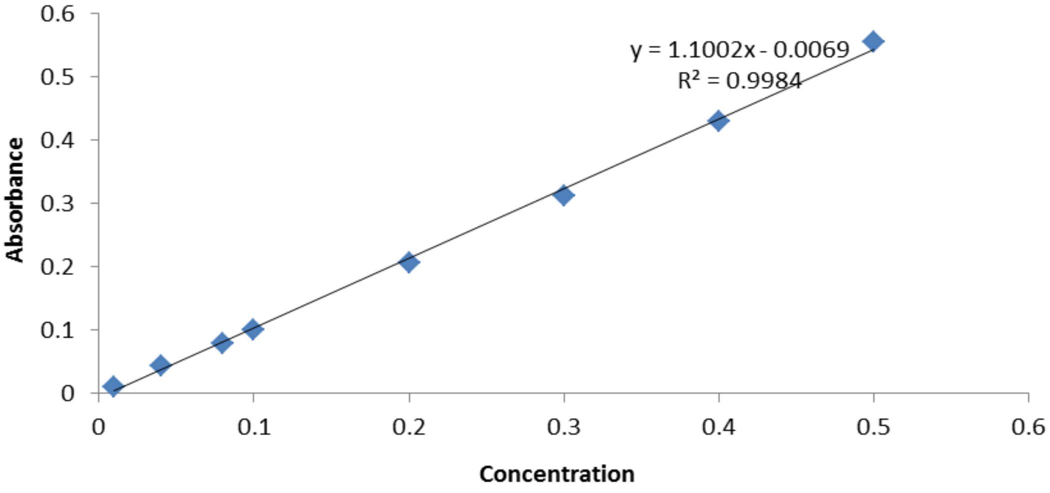

Figure (6): Calibration curve of cu(ii) solution.

4.3 Effect of Temperature

The effect of temperature was studied based on taking fixing values of some other variables that directly effect on (the dose of the adsorbent, pH, concentration and contact time), whereas the pH is 5, the adsorbent dose is 3.5 g, and the recall time was 60 minutes at 25°C, 35°C, 60°C and 80°C. The water bath was used to obtain different temperatures. Due to the increasing removal efficiency with temperature, the reaching of the maximum removal is 92% at 60°C with 80°C. The temperature-related to increasing in removal efficiency ,that can be attributed to the reactive and active sites, the removal process with increasing temperature is accompanied by a relative increase in the consumption of heating equipment for electricity and its conversion to heat in the water welding and the percentage of removal may be small compared to the normal temperature, as it was observed that the removal was equal to 85% at 25 degrees and the removal percentage is 95% at 60 and 80 degrees, as shown in Figure 7.

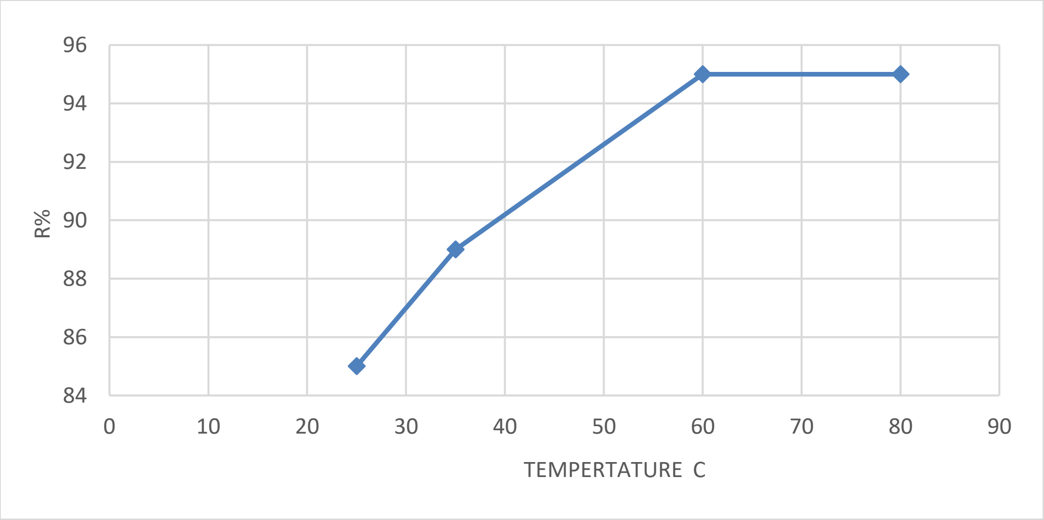

Figure (7): Effect of temperature on copper adsorption.

Condition: (adsorbent dosage =3.5 g concentration= 3000 ppm, pH=5, contact time=60 min, particle size = 0.075mm).

4.4 Effect of Particle Size

The measurement of adsorbent granules plays an important role in the transfer rate of metal ions from solution to adsorbent. In this work, different particle sizes were taken. The size of the fly Ash ranges from 0.075 to 0.5 mm, with all other parameters held constant (3000 ppm, pH = 5, T = 25 °C, dose = 3.5 g). Removal of copper ions, copper removal experiments were carried out using fly ash with different particle sizes (0.075-0.15-0.3-0.4-0.5) mm. This was done at room temperature (25 °C). The adsorbed ash was added at a dose of 3.5 g to react with copper ion solution for 60 min of contact time and pH 5. All other parameters were kept constant. The results obtained from the effect of the average adsorbed particle size on copper removal are shown in Figure 8. It is clear that the optimum average size of particle is 0.075 mm. It is observed that fly ash is capable of removing a high percentage of copper from aqueous solutions. The removal rates were 98.1%. For copper. Moreover, the copper removal rates decreased with increasing particle size. The removal rate at 0.3 mm particle size was 60.1%. At 0.5 mm particle size, the removal rate was 44.09%. These results can be attributed to. It is clear that the smaller the particle size, the greater the absorption capacity and this is explained by the presence and release of many active sites in fly ash.

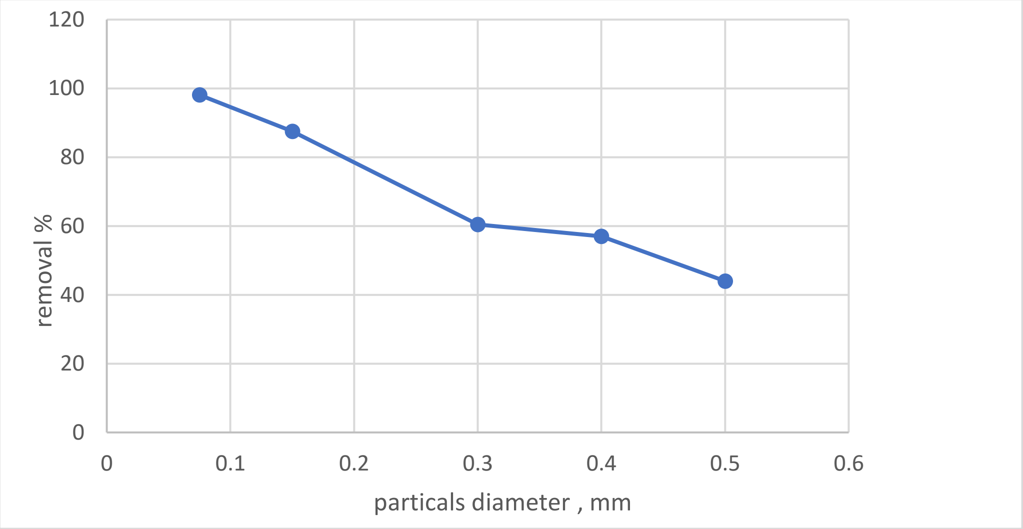

Figure (8): Effect of particle size on copper adsorption.

Condition: (adsorbent dosage =3.5 g, pH=5, concentration= 3000 ppm, time=60 min, and temperature 25 °C).

4.5 Thermodynamic Studies

Thermodynamic studies were carried out in presence of following conditions. Adsorbent concentration is 3.5 g/l; Cu (II) concentration 3g/l; at different rang of temperatures (25 °C, 35 °C, 60 °C and 80 °C). The thermodynamic parameters can be determined by using changes in the equilibrium constants with temperature. The thermodynamic parameters are (standard Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°)) which can be calculated with Eq. (3) to (6).

$$K_c = \frac{q_e}{C_e} \quad (3)$$

$$\Delta G^0 = -R\, T ln\, K_C \quad (4)$$

$$\Delta G^0 = \Delta H^0 - T\, \Delta S^0 \quad (5)$$

$$Ln\, K_C = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (6)$$

Where:

R is the universal gas constant= (8.314 J/mol °K) and, T is temperature (°K).

The K_c, q_e and C_e are the equilibrium constants, the Concentration of Cu (II) at the equilibrium and the amount of absorbed Cu (II) in the fly ash at equilibrium, respectively. These results of the calculations are shown in Table 4. The values of all temperature are ΔG°, which are negative and increasingly negative as the rising of fly ash's temperature. The spontaneous nature of the adsorption process is shown by negative values of ΔG°. The adsorption process is more advantageous at higher temperatures, as indicated by the decrease in the negative value of ΔG° with rising temperature.

Table (4): Thermodynamic variables for adsorption of Cu (II) onto fly ash.

T (OK)	ΔGO (J/mol)	ΔHO (J/mol)	ΔSO (J/mol oK)
298	-9546.91	53331.09	211.5
308	-9867.3		
333	-10668.2		
353	-11308.93		

When ΔH° is positive, the adsorption process must be endothermic. There are two types of adsorptions in the solid -liquid systems: first one the adsorption of species known as adsorbates, and the other one is the pre-adsorption desorption of water molecules. The adsorption process is endothermic, because the adsorbate needs to replace several water molecules in order to adsorb. ΔH° will therefore have a positive value. The magnitude of ΔH° can also be used to classify the types of sorption, therefore the value of physical adsorption heat ranges between 2100 and 20900 J/mol, and the heat of chemisorption usually is between 80000 and 200000 J/mol [24]. Moreover, a positive value of ΔS° indicates an adsorbent's affinity for the adsorbate, also it can be suggested as increased degree of uncertainty the interface of the solid/liquid during the adsorption process, which keeps the ions from escaping from the solid phase into the liquid phase. As a result, the amount of adsorbed of adsorbate will increase due to positive of ΔS°.

5. Conclusion

The findings from these studies highlight the significant capacity of fly ash as an effective adsorbent for the removal of ions from aqueous solutions. The efficiency of this adsorption process is primarily influenced by the chemical composition of the fly ash. The results demonstrate an increase in metal ion removal with rising temperatures, suggesting that thermal treatment enhances removal efficiency. However, achieving higher removal percentages through heating requires substantial energy input and incurs considerable construction and operational costs. Additionally, the results indicate that the removal efficiency improves as particle size decreases, with the highest removal rate observed at the smallest particle size (0.075 mm), attributed to the increased surface area available for adsorption. Thermodynamic analysis reveals that the adsorption of copper (Cu) ions is an endothermic process, both spontaneous and favorable under normal conditions. The positive value of ΔH° confirms that adsorption is more effective at elevated temperatures and supports the likelihood of chemical adsorption taking place with fly ash. In conclusion, this study establishes fly ash as a highly efficient adsorbent for the removal of metal ions from aqueous solutions, even in the presence of variables that may influence the adsorption process. Despite variations in operating conditions, fly ash has consistently proven to be an effective solution for metal ion removal.

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