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KINETIC STUDY FOR THE REMOVAL OF COPPER IONS BY FLY ASH/NaOH ADSORBENT

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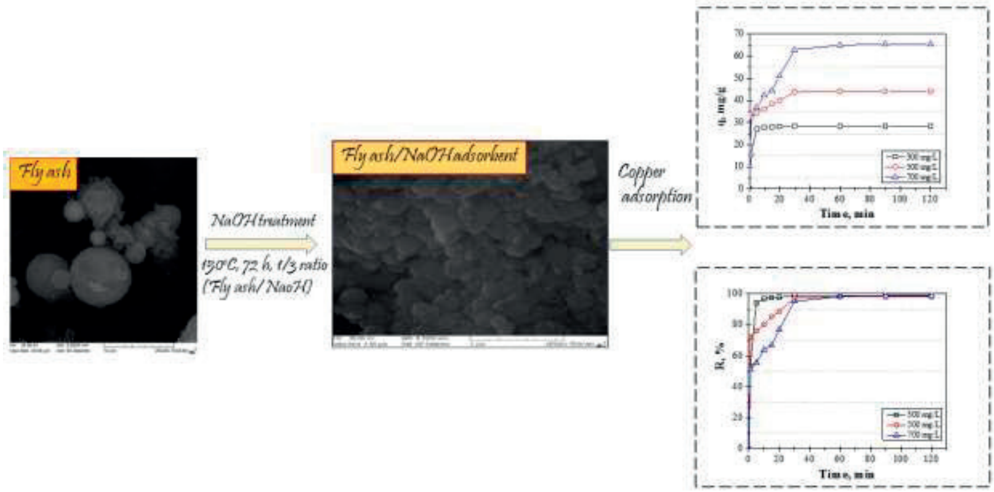
Abstract

The adsorption study of copper ions from aqueous solution using fly ash as a feed material was investigated. The proposed adsorbent was synthesized through the treatment of fly ash with NaOH at 150^{0}C, 72 hrs. The different parameters, such as: pH, dose of adsorbent, initial copper concentration, and contact time were examined. The adsorbent was characterized by SEM, EDX, XRD, FTIR, BET surface area, and thermal analysis. The copper adsorption process is very fast, a removal efficiency of 99% being reached in approx. 25 min. Three adsorption kinetic models presented in this paper: Pseudo first order, Pseudo second order, and Intraparticle diffusion model for describing the data were compared. The best model that described the kinetic data was the Pseudo second order kinetic model, Type 1. This research confirmed that the adsorbent prepared from fly ash, can be used successfully to remove copper ions from aqueous solution. The material prepared presents a high adsorption capacity for copper ions: 28.16 mg/g, 43.91 mg/g, and 65.15 mg/g for an initial copper concentration of 300 mg/L, 500 mg/L, and 700 mg/L.



Key words: *fly ash, synthesis, characterization, copper, adsorption, kinetic.*

INTRODUCTION

The removal of heavy metals from wastewater has been considered in many studies and represents a current trend (Noli et al., 2016; Buema et al., 2020; Forghani et al., 2020; He et al., 2020; Zhao et al., 2020; Mohammadi et al., 2021; Shahrashoub and Bakhtiari, 2021). Copper ions are classified as highly toxic metals. The toxic effects due to copper reported are diseases and disorders (Wu et al., 2018). The ability of different materials to eliminate copper ions from aqueous solution is often studied through adsorption technique, the other conventional methods being expensive.

The continuous produce of fly ash generated by power plants poses an environmental problem (Duan et al., 2016; Kankrej et al., 2018; Angaru et al., 2021). The capitalization of fly ash can be made in some applications, such as: cement industry, production of glass, zeolites, mesoporous materials, vitreous materials, and ceramics manufacture (Ahmaruzzaman, 2009). The current scientific research is focused is involvement of fly ash in synthesis of adsorbents for heavy metals removal due to its major chemical components: alumina, silica, ferric oxide, calcium oxide, magnesium oxide, and carbon (Sočo and Kalembkiewicz, 2013). Unfortunately, the fly ash shows lower adsorption capacity. For this reason, its activation has been proposed in order to improve its adsorption capacity. It is well known the fact that the synthesis conditions have a highly impact for the structure of the material obtained.

The pure-form zeolites A and X were synthesized from fly ash for copper and zinc removal. For the FA-ZA adsorbent, the adsorption capacity for Copper ions calculated from Langmuir isotherm was 82.74 mg/g (working conditions: adsorbent dosage 0.5 g, 25°C, pH 3.0). Zeolite A was more effective in removing Cu^{2+} and Zn^{2+} compared to zeolite X (Wang et al., 2009). Harja et al. studied copper ions removal from aqueous solutions by four new materials synthesized from Romanian fly ash by direct activation of ash with NaOH at 70^{0}C and 90^{0}C. The adsorption capacity was about 2 times higher compared to that of unmodified ash (Harja et al., 2012).

Zeolites synthesized from low and high calcium fly ash were tested for different heavy metals: Zn^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+} (Ji et al., 2017).

Zeolite Y synthesized from fly ash using the fusion-hydrothermal method has an adsorption capacity of 231.03, 248.29, and 250.71 mg/g at temperature of 301.15K, 318.15K, respectively 338.15K (Liu et al., 2019).

Qiu et al., in 2018, show that a maximum adsorption capacity of 27.55 mg/g is obtained by treating the fly ash with 1 mol/L Na_2HPO4, at a liquid-solid (solution/fly ash) ratio of 3 ml/g, 200ºC, 30 min.

A study by Darmayanti et al. (2019) for copper ions found the maximum adsorption capacity on two materials from fly ash was 40 mg/g.

Qiu reported the adsorption of copper ions using fly ash modified by microwave-assited hydrothermal process. The material obtained gave an adsorption capacity between 8.664 mg/g to 32.05 mg/g at an initial concentration range of 100-500 ppm (Qiu et al. 2019).

Vavouraki et al. have synthesized zeolite from Greek Fly Ash in order to be used as adsorbent for copper removal. Zeolites were synthesized through fusion of fly ash with NaOH or KOH (Vavouraki et al., 2020).

Using a material synthesized from fly ash with NaOH at room temperature, Buema et al. found that the maximum adsorption capacity of copper ions was between 27.32 to 58.48 mg/g (Buema et al., 2021a).

In this research, the fly ash was applied as feed material for the synthesis of a new adsorbent for the adsorption of copper ions. The basic characterization SEM, EDX, XRD, FTIR, BET surface area, and thermal analysis point of view was performed. The effect of different parameters, such as: pH, dose of adsorbent, initial copper concentration, and contact time was researched. Additionally, Pseudo first order model, Pseudo second order model (four types of its linearization), and Intraparticle diffusion model for describing the data were compared. The best model that described the kinetic data was the Pseudo second order kinetic model, Type 1.

MATERIALS AND METHODS

Materials

The fly ash used in this research with the aim to obtain a new material with the applicability in adsorption of copper ions from contaminated water was sourced from CET II Holboca (Iasi, Romania).

The chemical reagents were used as received.

The properties of the adsorbent including SEM, EDX, XRD, FTIR, BET surface area, and thermal analysis were performed using the following equipment:

- The morphology and the chemical composition were observed using Vega Tescan 3 SBH (Brno, Czech Republic), QUANTA 3D - AL99/ D8229 (FEI Company, Hillsboro, Oregon, USA);
- The material was characterized using X’PERT PRO MRD Diffractometer (PANalytical, Almelo, The Netherlands) in the 2θ range for phase determination.
- Fourier transform infrared spectroscopy (FT-IR) analysis was recorded on a Thermo

Scientific Nicolet 6700 FT-IR spectrometer. The investigation was performed over a wavenumber range of 4000-400 cm^{-1}

- Nitrogen adsorption/desorption isotherm was measured out at – 196°C on an Autosorb 1-MP gas sorption system (Quantachrome Instruments, Boynton Beach, FL, USA);
- The thermal analysis was performed with METTLER TOLEDO TGA/SDTA 851;
- The pH was measured with a pH-meter (Hanna Instruments, Cluj-Napoca, Romania), and the Spectrophotometer Buck Scientific was used for copper ions detection (Buck Scientific, East Norwalk, CT, USA).

Adsorbent synthesis

In short, 15 g of fly ash were mixed with 45 g of NaOH pellets and then the mixture was ground into powder that was kept at 150^0C for 72 h. After the NaOH treatment, the material obtained was washed several times with deionized water until neutral pH. Finally, the material was dried 24 hrs. at 60^0C.

Batch adsorption experiments

The stock solutions were prepared by dissolving appropriate amounts of $CuSO_4$ $5H_2O$ in distilled water. Copper concentration in the supernatant was analyzed spectrophotometrically. 0.1 M HCl or 0.1 M NaOH solution was used to adjust pH.

The adsorption experiments were carried out in order to investigate the effect of some experimental conditions: pH, contact time, dose of adsorbent, initial copper concentration. All the experiments were performed at room temperature under stirring at 300 RPM.

- Effect of pH: 2, 4, and 5; initial copper concentration = 500 mg/L, dose of adsorbent = 10 g/L;
- Effect of dose of adsorbent: *10 g/L (1 g ads/100 mL solution), 20 g/L (2 g ads/100 mL solution), and 40 g/L (4 g ads/100 mL solution),* initial copper concentration = 300 mg/L, the pH of the solution was kept constant at 5.
- Effect of initial copper concentration: *300 mg/L, 500 mg/L 700 mg/L,* dose of adsorbent = 10 g/L, pH = 5;
- Effect of contact time: *1-120 min,* initial copper concentration = 300, 500, 700 mg/L, dose of adsorbent = 10 g/L, pH = 5.

The quantity of copper ions adsorbed per gram of adsorbent and removal efficiency, R (%) were calculated based on the equations below:

$$q, mg/g = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$R, \% = \frac{(C_0 - C_e)}{C_0} x100 \quad (2)$$

Where C_0 and C_e are the initial and equilibrium copper concentrations (mg/L), q is the amount of copper adsorbed onto adsorbent (mg/g), V is the volume of copper solution (L), and m is the quantity of adsorbent (g).

RESULTS AND DISCUSSIONS

Characterization of adsorbent

SEM, EDX, XRD, FTIR, BET surface area, and thermal analysis measurements were used to characterize the prepared adsorbent. A comprehensive characterization is already presented in the literature (Buema et al., 2021b).

Effect of parameters

The adsorption process is controlled by several factors, such as: pH, dose of adsorbent, initial metal concentration, and contact time. All these parameters were taken into account in this research.

Effect of pH

In the first stage of the research, the pH influence was investigated. The interaction between copper ions and adsorbent is highly dependent on pH value. The adsorption capacity is generally improved with increasing of pH.

The effect of pH was investigated at 2, 4, and 5 (Figure 1). No higher pH values were used to avoid precipitation.

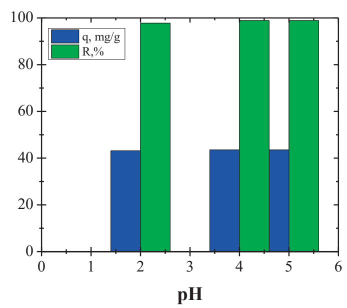


Figure 1. Effect of pH on the adsorption capacity and the removal efficiency

Copper ions adsorption was found to be 43.15 mg/g, 97.77% at pH 2, respectively 43.53 mg/g, 98.88% at pH values of 4 and 5. Similar observation has been reported in the literature for adsorbents based on ash synthesized by direct activation, but at lower temperatures (Buema et al., 2021a). So, it can be concluded that the adsorption capacity, respectively the removal efficiency values remain constant at pH 4 and 5.
Therefore, the effect of the other parameters was determined at pH of 5.

Effect of dose of adsorbent

This parameter was investigated by increasing the dose of adsorbent from 1 to 4 g adsorbent/100 mL solution. The data can be consulted in the Figure 2.

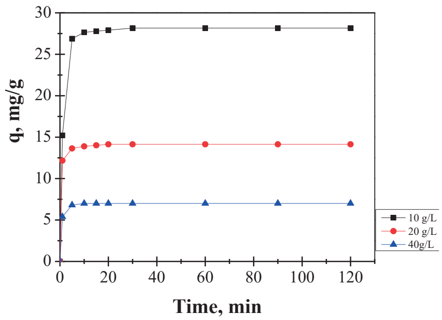


Figure 2a. Effect of dose of adsorbent on the adsorption capacity

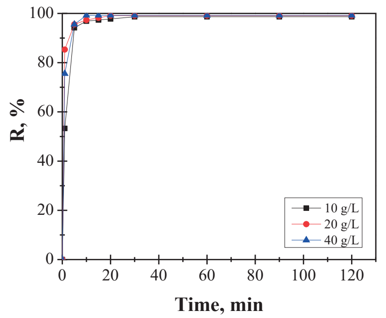


Figure 2b. Effect of dose of adsorbent on the removal efficiency

In the previous study it was reported that the copper adsorption capacity depends on dose of adsorbent. The results show that an increase in the adsorbent dose determines a lower value of the adsorption capacity. On the other hand, removal efficiency values of approx. 99% can be obtained by using adsorbent doses ratio of 1 g/100 mL, 2 g/100 ml, and 4 g/100 ml.
By using 10 g/L of adsorbent (1 g/100 mL) the adsorption capacity is higher compared with those observed at 20 g/L (2 g/100 ml) and 40 g/L (4 g/100 ml). However, the tests highlight that copper ions were rapidly removed, after 25 min the equilibrium being reached in all three cases.

Effect of copper initial concentration and contact time

The initial metal concentration presents a significant impact through adsorption capacity and removal efficiency (Hamid et al., 2020; Claros et al., 2021).
Conform to Figure 3a, a high maximum adsorption capacity of 65.15 mg/g was observed at 700 mg/L initial copper concentration compared to that of 300 mg/L initial copper concentration, 28.16 mg/g. As shown above, copper ions were rapidly adsorbed. No significant adsorption was observed after 60 min. of contact time.

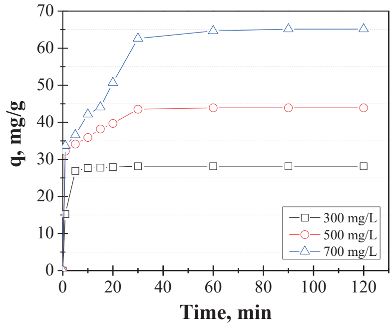


Figure 3a. Effect of initial copper concentration on the adsorption capacity

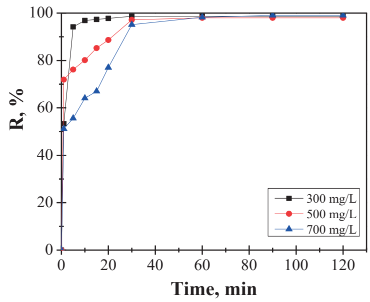


Figure 3b. Effect of initial copper concentration on the removal efficiency

Kinetics study

To obtain information regarding the adsorption mechanism of the modified fly ash, the experiments of kinetics were investigated. Pseudo first order model, Pseudo second order model, and Intraparticle diffusion model are typical for analyzing the adsorption kinetics in the solid/liquid system (Yang et al., 2019; Bashir et al., 2020).

The results are presented in Figures 4, 5 and 6, respectively in Table 1.

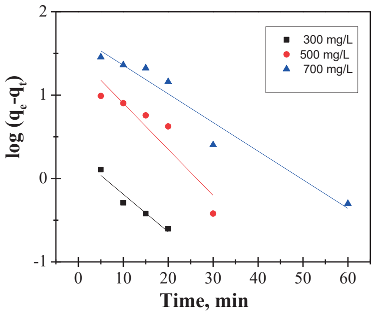


Figure 4. Pseudo first order model

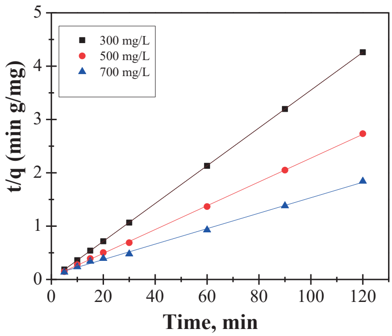


Figure 5. Pseudo second order model

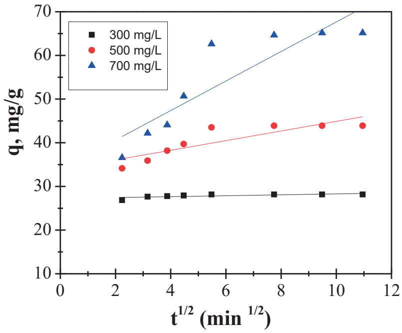


Figure 6. Intraparticle diffusion model

The kinetic equations are presented in eq. 3, 4 and 5.

$$\log(q_e - q_t) = \log q_e - \frac{(k_1 t)}{2.303} \quad \text{..............(3)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \quad (4)$$

$$q_t = k_i t^{0.5} + c \quad \text{..............................(5)}$$

From the data presented in Table 1, the correlation coefficients (R^2) of the Pseudo second order model are generally higher than the other two investigated models.

The experimental q_e values of 28.16, 43.91, and 65.15 mg/g for 300, 500, and 700 mg/L are in agreement with the q_e value of 28.25, 44.84, 68.96 and mg/g calculated from the Pseudo second order model.

Based on this, Pseudo second order model was linearized to four different forms. The results are given in Figures 7-9. Parameters including qe, k_2, and R^2 are listed in Table 2.

Analyzing the data presented in Table 2, it can be noted that the values of R^2 for Types 2, 3 and 4 were lower than 0.89. Therefore, the good correlation with the experimental data is for the Pseudo second order model, Type 1.

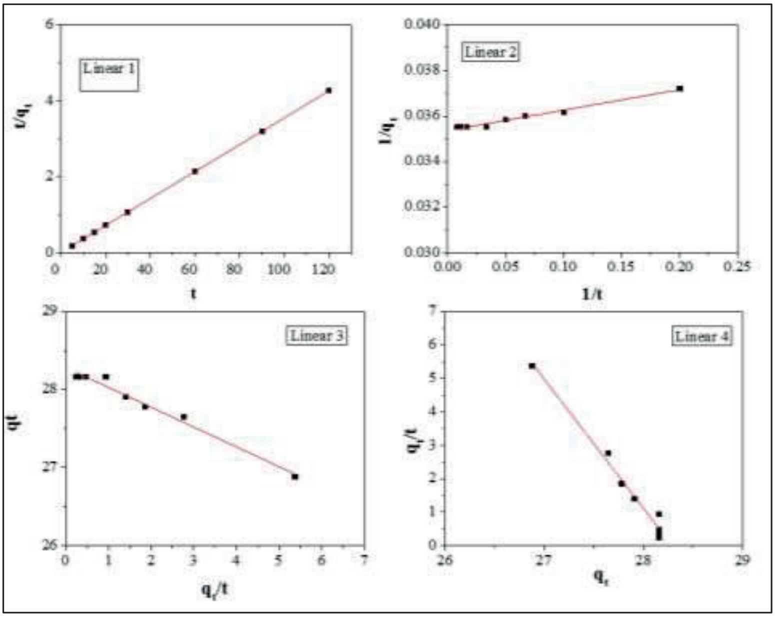


Figure 7. Pseudo second order (Type 1-Type 4) plot of copper ions, 300 mg/L

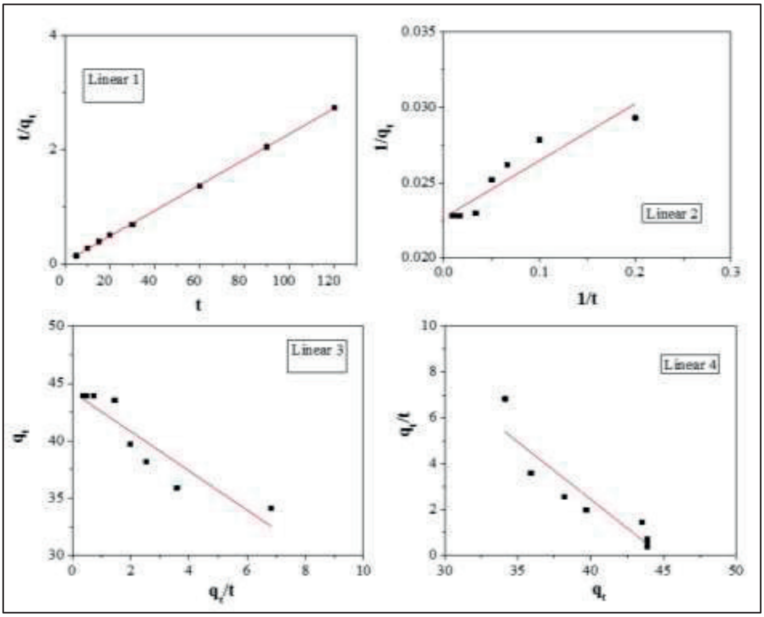


Figure 8. Pseudo second order (Type 1-Type 4) plot of copper ions, 500 mg/L

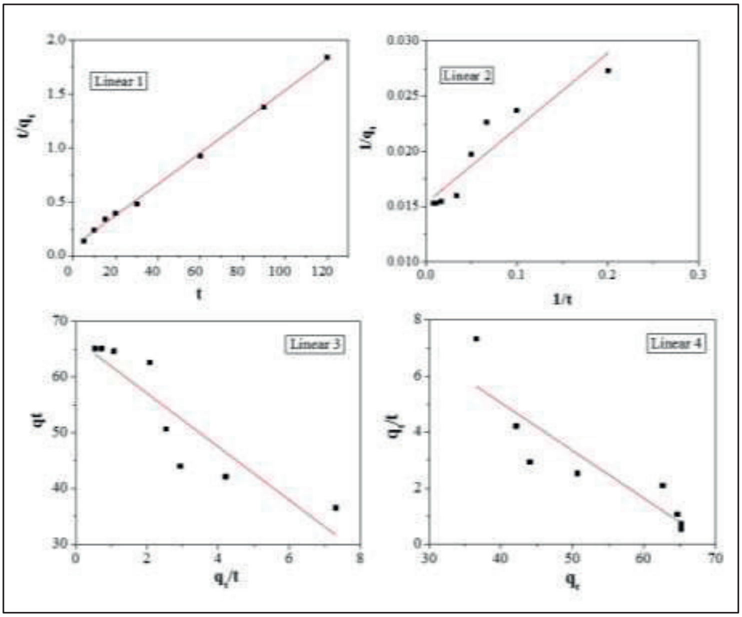


Figure 9. Pseudo second order (Type 1-Type 4) plot of copper ions, 700 mg/L

Table 1. The relevant parameters of the kinetic models

	Pseudo fist order		Pseudo second order			Intraparticle diffusion model		
	k_1, 1/min	R^2	k_2, g/mg min	qe, mg/g	R^2	ki, mg/g·min$^{0.5}$	c	R^2
300 mg/L	0.1038	0.9381	0.1843	28.25	1	0.1054	27.232	0.5587
500 mg/L	0.1273	0.8659	0.0114	44.84	0.9997	1.1035	33.86	0.7539
700 mg/L	0.0789	0.9508	0.0025	68.96	0.9981	3.3807	33.85	0.7978

Table 2. Kinetic constants for Pseudo second order model, Type 1-Type 4

Kinetic type	Parameters	Values		
		300 mg/L	500 mg/L	700 mg/L
Type 1 q_e = 1/m k = m^2/c	k_2, g mg/min	0.1843	0.0114	0.0025
	qe, mg/g	28.25	44.84	68.96
	R^2	**1**	**0.9997**	0.9981
Type 2 q_e = 1/c k = c^2/m	k_2, g mg/min	0.1394	0.0136	0.0034
	qe, mg/g	28.25	44.05	65.4
	R^2	0.9822	0.8824	0.8786
Type 3 q_e = c k = -1/c x m	k_2, g mg/min	0.0089	0.0388	0.0717
	qe, mg/g	28.281	44.26	66.716
	R^2	0.9807	0.8592	0.8173
Type 4 q_e = -c/m k = m^2/c	k_2, g mg/min	0.1365	0.0111	0.0024
	qe, mg/g	28.287	44.89	69.56
	R^2	0.9807	0.8592	0.8173

CONCLUSIONS

The following conclusions can be drawn based on the above study:

- The fly ash was used in order to obtain a new material with applicability in copper ions adsorption.
- The full characterization of the material is described as well as the adsorption study of copper ions from aqueous solution.
- The new adsorbent tested in copper adsorption was synthesized through the treatment of fly ash with NaOH at 150^{0}C, 72 hrs and it was characterized by SEM,

EDX, XRD, FTIR, BET surface area, and thermal analysis.

- The different parameters: pH, dose of adsorbent, initial concentration, and contact time were examined.
- The removal efficiency of 99% is reached in approx. 25 min.
- Three adsorption kinetic models were applied in this paper. The highest correlation coefficients, R^2, were obtained for the Pseudo second order kinetic model.
- Finally, this research confirmed that the adsorbent prepared from fly ash, can be used successfully to remove copper ions from aqueous solution, with a maximum adsorption capacity of 28.16, 43.91, and 65.15 mg/g for 300, 500, and 700 mg/L.

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