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# Low cost adsorbents obtained from ash for copper removal

**Maria Harja*, Gabriela Buema*†, Daniel-Mircea Sutiman*, Corneliu Munteanu**, and Daniel Bucur*****

*Faculty of Chemical Engineering and Environmental Protection, Gheorghe Asachi Technical University of Iasi, Prof.dr.doc. Dimitrie Mangeron 73, Iasi 700050, Romania
**Faculty of Mechanic Engineering, Gheorghe Asachi Technical University of Iasi, Prof.dr.doc. Dimitrie Mangeron 67, Iasi 700050, Romania
***University of Agricultural Sciences and Veterinary Medicine in Iasi, M. Sadoveanu 3, Iasi 700490, Romania
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**Abstract**−We investigated the utilization of ash and modified ash as a low-cost adsorbent to remove copper ions from aqueous solutions such as wastewater. Batch experiments were conducted to determine the factors affecting adsorption of copper. The influence of pH, adsorbent dose, initial $Cu^{2+}$ concentration, type of adsorbent and contact time on the adsorption capacity of $Cu^{2+}$ from aqueous solution by the batch adsorption technique using ash and modified ash as a low-cost adsorbent were investigated. The optimum pH required for maximum adsorption was found to be 5. The results from the sorption process showed that the maximum adsorption rate was obtained at 300 mg/L when a different dosage of fly ash was added into the solution, and it can be concluded that decreasing the initial concentration of copper ion is beneficial to the adsorption capacity of the adsorbent. With the increase of pH value, the removal rate increased. When the pH was 5, the removal rate reached the maximum of over 99%. When initial copper content was 300 mg/L and the pH value was 5, the adsorption capacity of the zeolite Z 4 sample reached 27.904 mg/g. The main removal mechanisms were assumed to be the adsorption at the surface of the fly ash together with the precipitation from the solution. The adsorption equilibrium was achieved at pH 5 between 1 and 4 hours in function of type of adsorbent. A dose of 1 : 25 g/mL of adsorbent was sufficient for the optimum removal of copper ions. For all synthesized adsorbents the predominant mechanism can be described by pseudo-second order kinetics.

Key words: Adsorption Capacity, Ash, Copper ions, Kinetic, Zeolite

## INTRODUCTION

It is known that heavy metal ions are the most common pollutants in several industrial wastewaters [1]. The presence of the toxic metals generated by metal finishing or mineral processing industries can result in major hazards to the environment and public health [2-4]. The discharge of large amounts of such wastewaters into water resources affects the physical and chemical properties of receiving waters [5,6]. Many electroplating and printed circuit board factories discharge large amounts of poisonous heavy metals in their wastewater, with copper ions being one of the most common [7]. Copper and its compounds are widely used in many industries and there are many potential sources of copper pollution. The continued intake of copper by humans leads to necrotic changes in the liver and kidney, mucosal irritation, wide spread capillary damage, depression and gastrointestinal irritation [8]. The CMA (concentration maximum admissible) of copper in drinking water is 0.1 mg/L [9]. But, there is a considerable need to treat industrial effluents containing such heavy metals prior to discharge to protect public health. The metal needs to be removed from industrial effluents before discharge into the environment to mitigate any impact on plant, animal and human receptors [8].

During recent years, the methods that have been utilized for the removal of heavy metals from wastewaters include chemical precipitation, ion-exchange, electro-dialysis, reverse osmosis, membrane filtration and adsorption. One of the processes for removal of heavy metals from wastewater with low cost is adsorption [10-12].

Many have proposed the different adsorption abilities of various low-cost adsorbents (such as carbonates, phosphate rocks, bentonite, lignin, clay minerals, fly ash, blast furnace sludge, red mud, zeolites, biomass and bagasse fly ash) for the removal of heavy metals from wastewater [6,7,11,13].

Coal fly ash is a mineral waste from coal-burning power plants. In 2008 in Romania, coal provided 42.5% of the total supply of electric power to generate electricity. Besides, worldwide production of coal fly ash is ca. 500 million tons by product per year [14]. This waste must be reduced prior to disposal. Thus, the ash from power plants may be recycled in various fields such as stabilization of soils, fertilization of soil, production of geopolymers, in building industry as a bottom layer in road construction etc. [14-18]. In the recent past, many researchers have used fly ashes and modified ashes from alkaline or acid attack as adsorbents for wastewater. Primary fly ash and secondary zeolite from ash are materials that have been extensively studied and approved as good absorbents [11,19-22]. The results of this material have two benefits: the lack of need for disposal of ash, which is a waste product, and its usage as a low cost adsorbent for the treatment of flue gas, wastewater and polluted soils [20].

The activation of ashes can be realized by three methods: direct hydrothermal conversion, diffusion and wave diffusion [23]. In this study we proposed the direct conversion method, at a temperature that is relatively low for obtained zeolitic material with adsorption

†To whom correspondence should be addressed.
E-mail: buema_gabrielaa@yahoo.com

capacities for copper ions. The influence of different factors on the adsorption process has also been studied.

## EXPERIMENTAL

The ash and the zeolitic materials were characterized from a granulometric distribution with a SALD-7001 diffractometer with a laser. The chemical and the mineralogical characterizations were performed with the following equipment:

- SEM/EDX for morphology and elementary analysis of the ashes samples. The samples were studied with a QUANTA 3D - AL99/D8229;
- Diffractometer X'PERT PRO MRD;
- Multi-Parameter Consort C831;
- Spectrophotometer Buck Scientific for heavy metal detection by atomic spectroscopy.

Adsorption isotherms were determined using the batch equilibrium method. The adsorption of Cu(II) was studied after adding 2 g of adsorbent into 200 mL of aqueous solution containing the desired Cu(II) concentration (300-700 mg $L^{-1}$), adjusting the pH of the solution to between 2 and 6, and shaking at 300 rpm for 8 hours at 20 °C in a reciprocating shaker, after which the samples were filtered and analyzed. The residual concentration of copper ions was determined by atomic absorption spectrometry. The heavy metal ion used within this investigation was the $Cu^{2+}$ ion from a copper sulfate solution. The ash/solution ratio was equal to 1 : 50 for the considered pH values. At certain time intervals, samples were collected, filtered and analyzed by atomic absorption in order to establish the content of copper ions.

The adsorption capacity was defined as a percentage and calculated by the adsorption capacity equation (Eq. (1)):

$$R\% = \frac{m_0 - m}{m_0} \cdot 100 \quad (1)$$

where $m_0$ - pollutant mass, in solution, at the initial moment (mg), and m - pollutant mass, in solution, at the sampling time (mg). The conditions used for synthesis of zeolite are presented in Table 1. After treatment, the synthesized samples were crystallized for 18 hours at ambient temperature, then filtered, washed and dried.

## RESULTS AND DISCUSSION

### 1. Ash Characterization

The results of the granulometric distribution are presented in Fig. 1. It can be observed that the mean particles are 0.2 μm.

From the SEM analysis for ash the variation domain of particle granulometry can be observed (Fig. 2). Also, it is obvious that the sample has spherical particles and small quantities of irregular shape

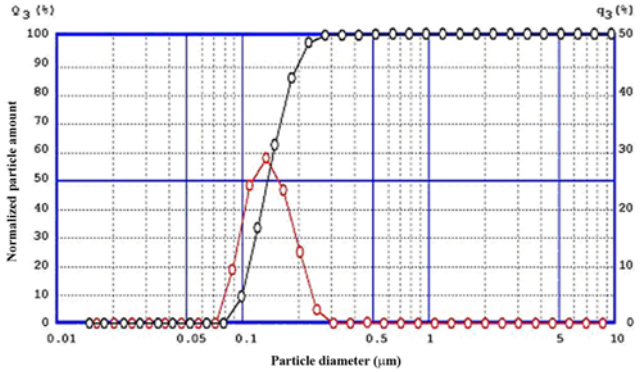


**Fig. 1. Granulometric distribution for ash.**

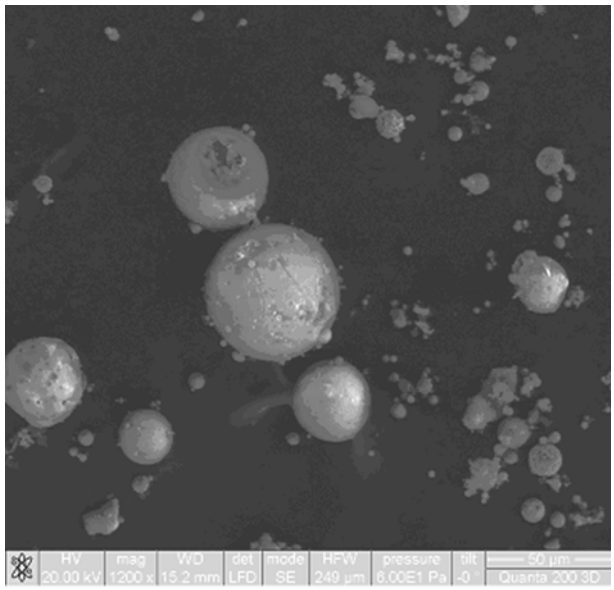

**Fig. 2. Scanning electronic microscopy image for ash.**

of the particles, due to the presence of unburned carbon. Morphology is in accordance with the literature [6, 11].

The physico-chemical and technological characterizations of the ash have shown that regardless of the source, the ash has the following as principal elements: Si, O, Al, Ca, Fe, K, Mg, N, C and small quantities (under 1%) of Ti (Fig. 3), in accordance with the data reported in literature [24].

The quantities of each element are: Si - 34.48%, O - 27.91%, Al - 11.99%, C - 7.97%, Fe - 6.94%, Ca - 3.96%, K - 2.56%, Mg - 1.88% and N - 1.76%.

XRD as seen in Fig. 4 shows that the ash contains crystalline phases: quartz (Q), illite (I), kaolinite (K), mullite (Mu), hematite (He), mus-

**Table 1. Conditions of zeolite synthesis**

| | | NaOH concentration | Ratio | Temperature | Time |
|---|---|---|---|---|---|
| Z 1 | 60 g fly ash+180 mL NaOH | 2 M | 1/3 | 70 °C | 4 hours |
| Z 2 | 60 g fly ash+180 mL NaOH | 2 M | 1/3 | 90 °C | 4 hours |
| Z 3 | 60 g fly ash+300 mL NaOH | 5 M | 1/5 | 70 °C | 4 hours |
| Z 4 | 60 g fly ash+300 mL NaOH | 5 M | 1/5 | 90 °C | 4 hours |

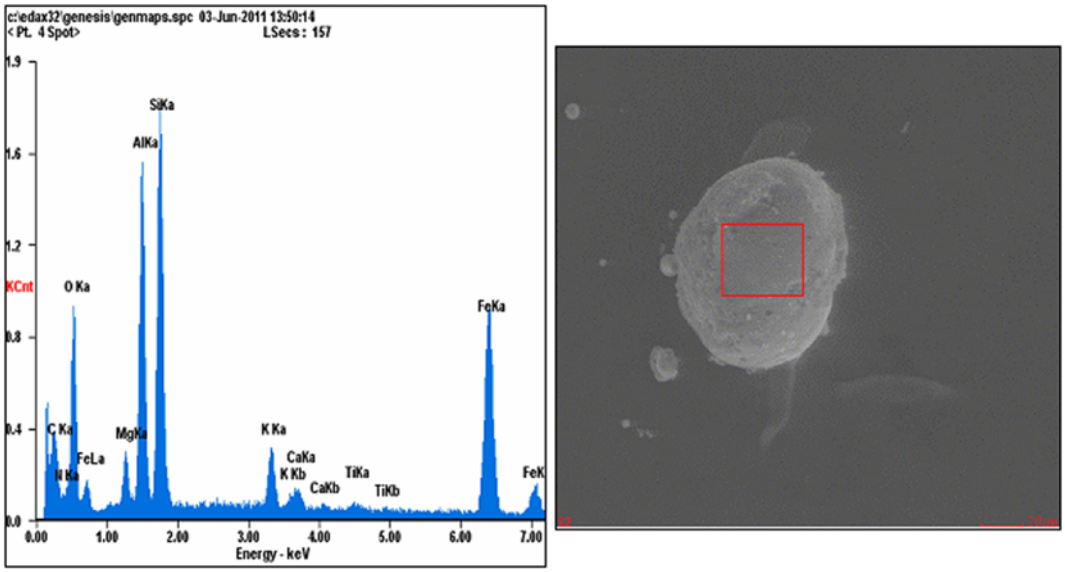


**Fig. 3. Chemical composition of ash.**

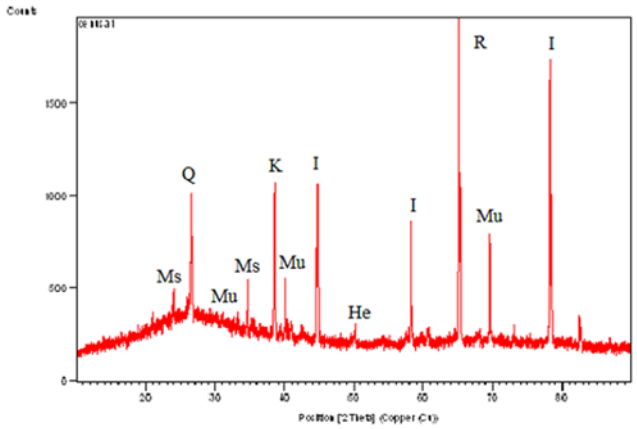


**Fig. 4. XRD Spectrum for ash.**

covite (Ms), rutile (R) and a glassy phase [25].

The elements existing in the glassy phase of ash are estimated by XRD cooperating with EDX indicating the presence of Si, Al and some alkalis such as Ca and K.

## 2. Adsorbent Characterization

SEM images show that the zeolite presents modified particles (Fig. 5) compared to the fly ash (Fig. 2). The unmodified ash consists of spherical and irregular shaped particles, while the zeolite has marked changes in the surface morphology due to the alkali activation.

It can be observed that the increase of the solid/liquid ratio and NaOH concentration determined the highest degree of zeolitization.

The synthesized zeolites were chemically analyzed. The analysis shows that the main constitutive elements of the zeolites are the same in ash, but the quantities of Na are greater. Taking into account that the synthesis has been performed with sodium hydroxide; the calcium content decreases when this element is replaced by sodium within the zeolite structure, Fig. 6.

XRD analysis was employed to establish the crystalline phase. In the case of zeolite Na-P1 are obtained [26,27].

## 3. Adsorption of $Cu^{2+}$ Ions from Solutions

The experimental research aimed at establishing the kinetics of $Cu^{2+}$ removal from aqueous solutions. The metal ions can be removed from aqueous solutions by precipitation or adsorption. In fact, a number of studies were conducted to show the effectiveness of ash in the removal of heavy metal ions from aqueous solutions.

### 3-1. Effect of pH

For the adsorption study we established the pH influence. The pH is one of the most important factors which control the copper adsorption on the ash and zeolites. The copper removal efficiency was investigated for pH values of 2, 4, 5 and 6, where the chemical precipitation values are avoided. The influence of pH was a study for raw ash and for zeolite. Adsorption of $Cu^{2+}$ onto the ash and zeolites (500 mg $L^{-1}$) was studied at various pH values to optimize the removal of $Cu^{2+}$ at 20 °C. It is evident that the uptake was low at lower pH values; however, with increasing pH, a significant enhancement in the adsorption was recorded. The optimum pH for the removal of $Cu^{2+}$ was found to be in the range 4.5-6.0, with a removal of about 99.6% $Cu^{2+}$ from the solution.

The data concerning the influence of pH on the removal of $Cu^{2+}$ is presented in Fig. 7. From Fig. 7 it can be observed that the capacity of adsorption increases with increase of pH value. At pH 2 the ash and Z 1 do not remove the $Cu^{2+}$ ions. For the unmodified ash after 8 hours the adsorption capacity is about 28% at pH 5, and the maximum value is 35% after 24 hours. At pH 5 the Z1 maximum value is 90% at 5 hours, and in the case of Z 4 an adsorption capacity of 99% at 2 hours is obtained.

For zeolite Z 2 the smallest value of process efficiency (18%) is registered at pH=2, while the maximum removal percent (92%) result is for values of pH 5. In the case of zeolite Z 4, a maximum value of 97% is registered at all values of pH, but in 120 minutes at pH 5 and 450 minutes at pH 2, Fig. 8.

The results show high removal efficiency of over 97% of copper onto zeolite at pH value 5.

The pH value of the solution could affect the surface electricity

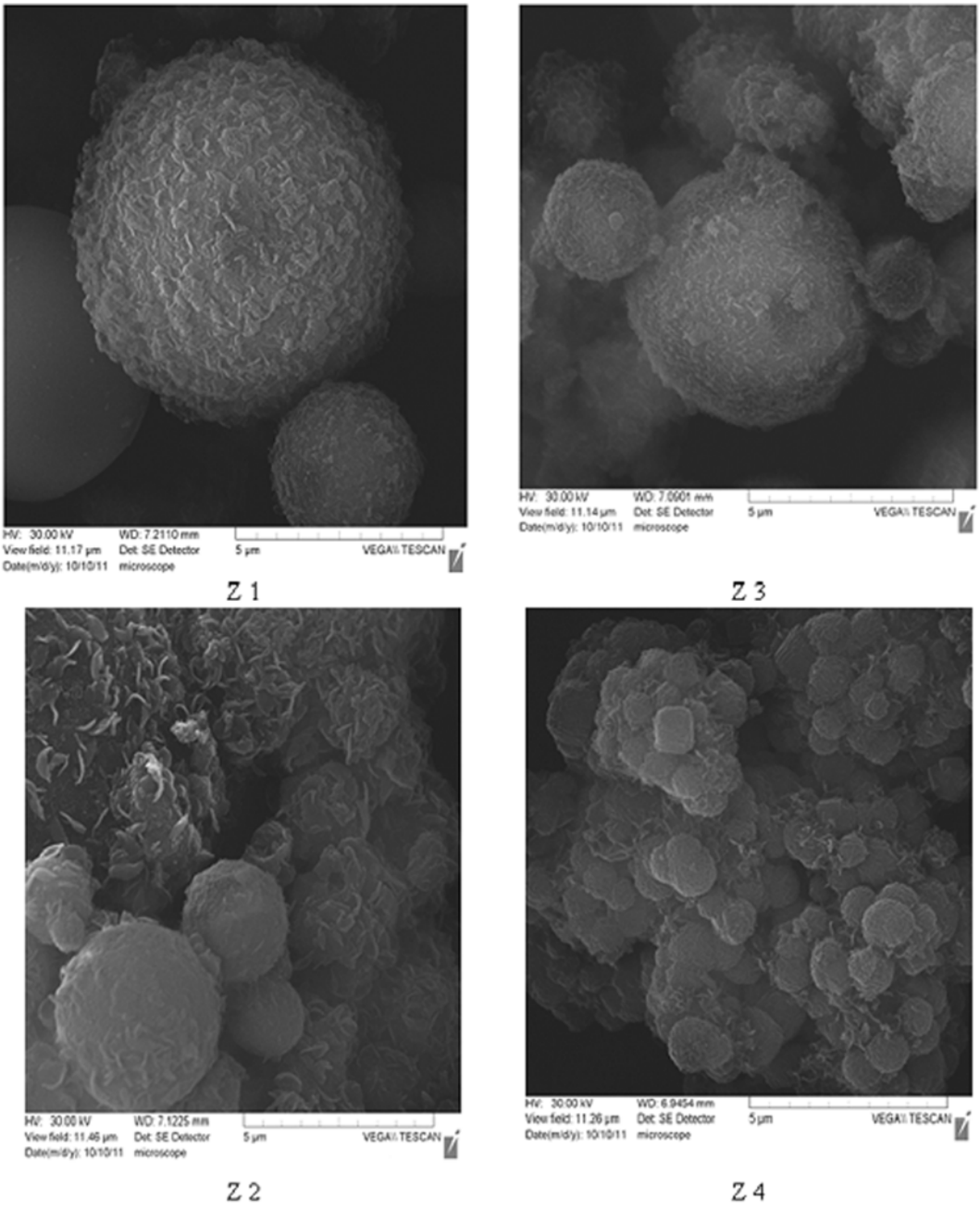


**Fig. 5. Scanning electronic microscopy image for synthesized zeolite.**

property of adsorbent, ionic strength and the existing form of metal ions in the solution. The low adsorption capacity at pH values below 4 can be attributed to hydrogen ions that compete with the metal ions for the adsorption sites. At pH values higher than 6, the copper ions precipitated as its hydroxide, which decreased the rate of adsorption and subsequently the percent removal of metal ions.

Therefore, under the strong acidic condition, the $H^+$ ions in the solution could neutralize the basic anhydride on the surface of the adsorbent, which decreases the adsorption ability. On the other hand, under the strong alkaline condition, precipitation could occur, which may inhibit the adsorption process. The mechanism of removing copper ions from the aqueous solution was assumed to be a combination of the adsorption at the surface of the adsorbent together with the precipitation from the solution, in accordance with literature [28].

3-2. Effect of Type of Adsorbent

The efficiency of the removal of $Cu^{2+}$ on the studied ash and zeolite at pH 5 is exhibited in Fig. 10. According to the results presented in Fig. 9, at the initial concentration of copper ions of 300 mg/mL, Z4 has the greatest capacity of adsorption: 98% in 120 minutes of contact. On the other hand, the lowest capacity is presented by unmodified ash: only 40% after 450 minutes of contact.

3-3. Effect of Initial Concentration of the Copper on the Adsorption Process

The experiments were performed using an adsorbent and a copper solution, for which the same ratio was kept. Thus, for this study

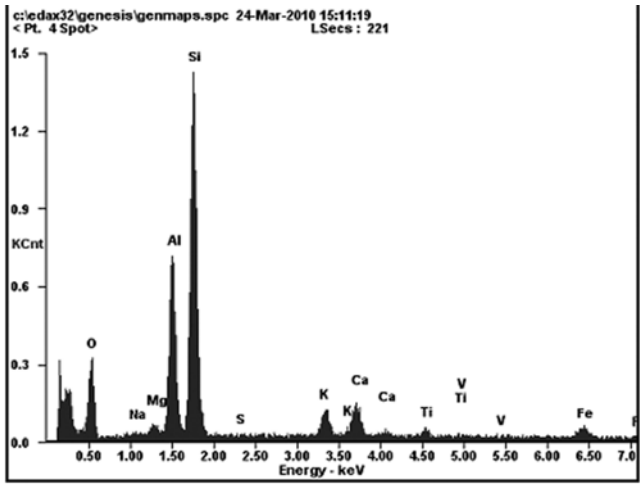


**Fig. 6. EDX analysis of zeolite.**

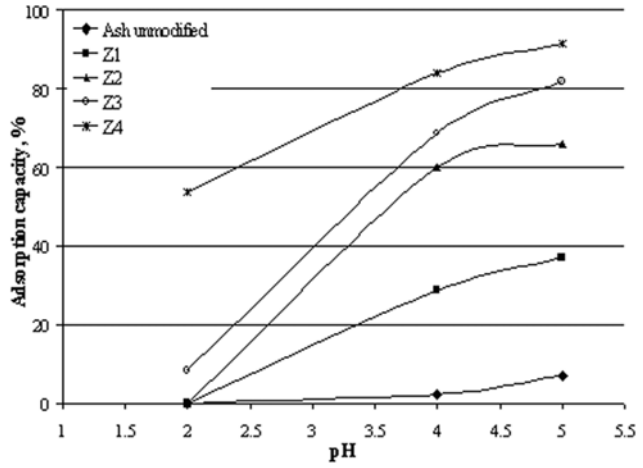


**Fig. 7. Influence of pH on copper adsorption capacity onto the ash.**

three solutions of copper, with initial concentrations of 300 mg $L^{-1}$; 500 mg$L^{-1}$ and 700 mg $L^{-1}$ have been used.

The results for unmodified ash are presented in Fig. 10.

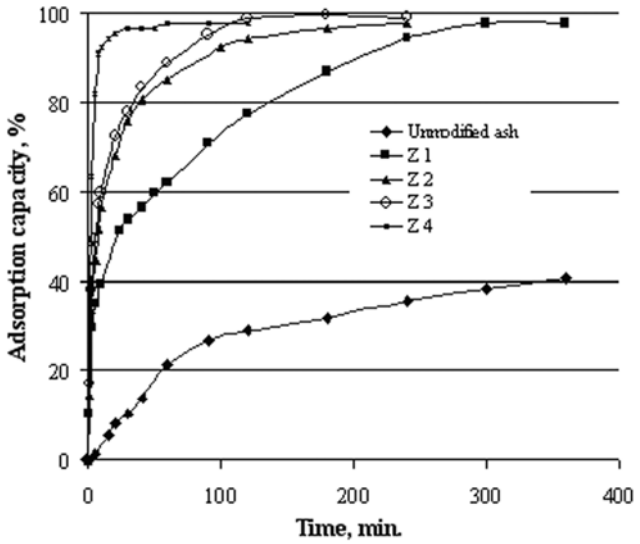


**Fig. 9. Influence of type of adsorbent at pH 5, $C^o$=300 mg/mL.**

From Fig. 10 it can be observed that with the increasing concentration from 300 to 700 mg/L, the adsorption capacity of copper ion decreases. The adsorption performance of the ash surface was shown and the maximum adsorption rate was obtained at 300 mg/L. From Fig. 10, it could be concluded that decreasing the initial concentration of copper ion is beneficial to the adsorption ability of fly ash, in accordance with [28,29].

The same trend was obtained for zeolites material (Fig. 11): with the copper ion concentration increased from 300 to 700 mg/L, the tendency of removal rate decreased. In Fig. 11 the adsorption performance of the fly ash surface is shown; the maximum adsorption capacity of 99% was obtained at 300 mg/L, in accordance with [28].

The process appears as being very fast at the beginning because a big amount of copper is retained in the first 60 minutes. This behavior can be explained by the strong attraction between the positive charge of the copper and the negative sites from the adsorbent material. The results show the decrease of the process efficiency with the increase of the initial concentration of the copper as a result

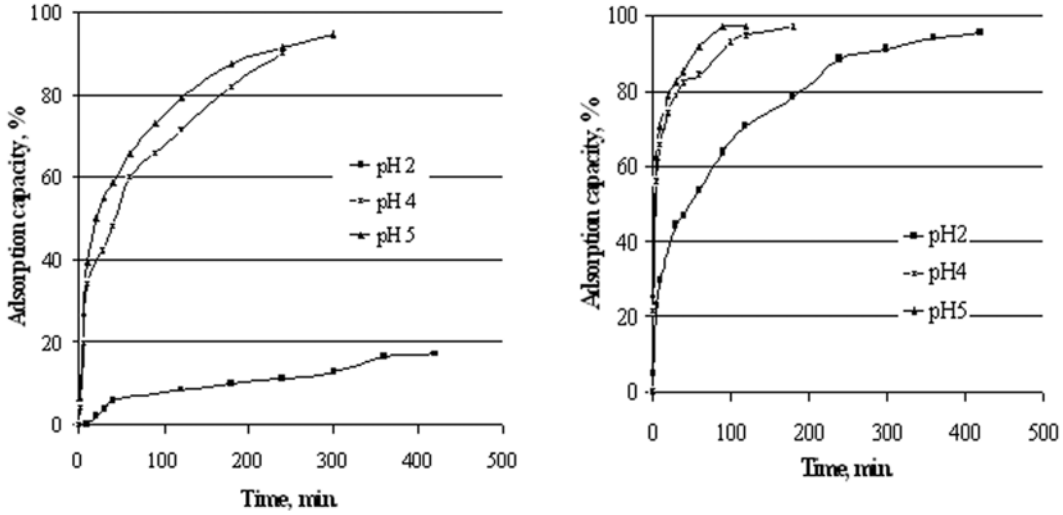


**Fig. 8. Influence of pH over copper removal; T=293 K, adsorbent dosage 1 : 100, C=500 mg/L.**

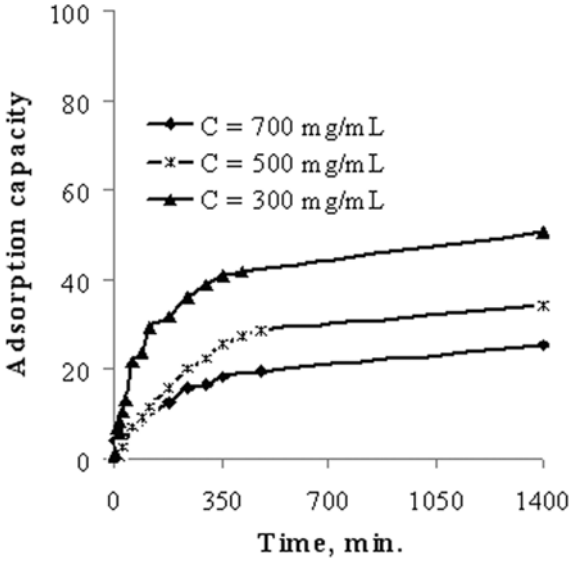


**Fig. 10. Influence of initial concentration on the adsorption process.**

of saturation with copper ions of the active sites from the structure of the adsorbent.

3-4. Effect of Contact Time

The results of the effect of equilibrium time on the sorption of $Cu^{2+}$ onto different adsorbents are shown in Fig. 12.

Fig. 12 clearly shows that the adsorption of $Cu^{2+}$ ions onto the zeolite was relatively fast and the complete adsorption equilibrium between the two phases was obtained after different times, in the function of type of adsorbent. The results show that one hour was a sufficient time for copper adsorption onto the zeolite Z 4. In the case of the Z3, the maximum value for adsorption was after 2 hours. This zeolite has a different temperature of synthesis (70 °C). If the concentration of the NaOH solution is 2 M (Z 1 and Z 2) the maximum value of adsorption capacity is obtained after 3, respectively 4 hours of contact. The ash has maximum value of adsorption of about 40% after 6 hours of contact. The increase of quantities of copper removes and decreases the contact time, for the same adsorption capacity justified modified of ash. The fast ion uptake by the adsorbents may be attributed to their large surface area for the sorption of the metal ions onto the binding sites. Thus, for subse-

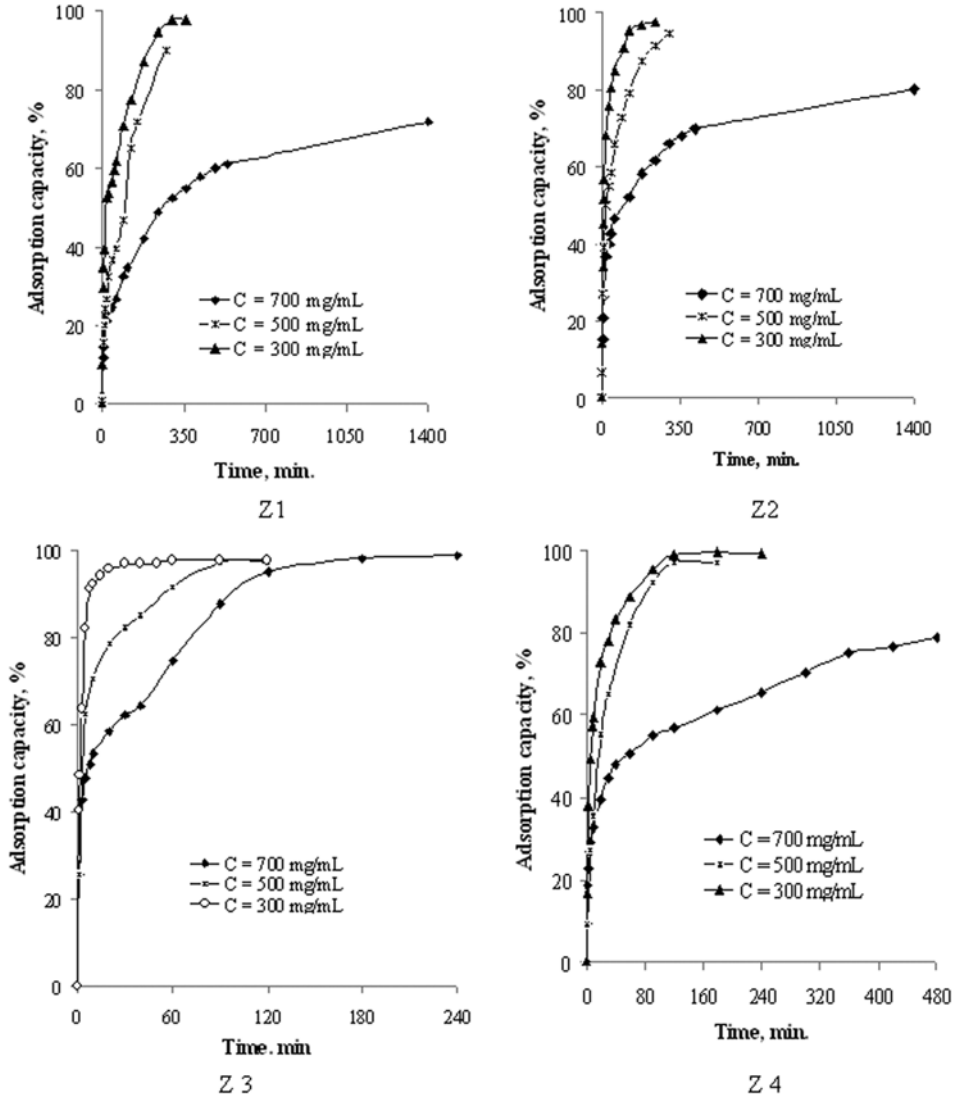


**Fig. 11. Influence of initial concentration on the adsorption process, zeolites, pH=5.**

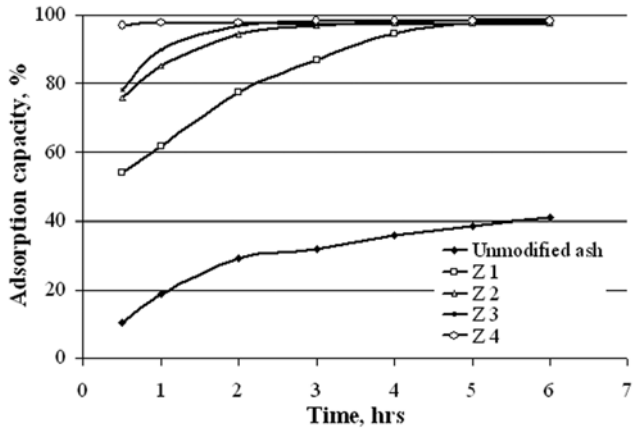


**Fig. 12. Influence of contact time on the adsorption process, pH=5.**

quent experiments, a contact time of 2, respectively 3 hours was chosen for the sake of convenience.

3-5. Effect of Adsorbent Dose

The adsorption capacity of copper ions is a function of adsorbent dosage. The efficiency of the ash and modified ash was evaluated at different doses using the adsorption capacity of copper. The experiments were conducted at a constant initial $Cu^{2+}$ concentration (500 mg $L^{-1}$), contact time (4 hours), temperature (20±1 °C), and stirring speed (300 rpm) with varying adsorbent doses (1 : 25-1 : 100 g $mL^{-1}$). The measurement of adsorption of $Cu^{2+}$ as a function of time at different doses of ash indicated that the removal of copper increased with increasing adsorbent dose (Fig. 13).

The increase in copper removal with ash dose can be attributed to the increased surface area and the availability of more adsorption sites. The adsorption capacity was found to increase proportionally with the amount of ash. Therefore, 1 : 25 g $mL^{-1}$ of adsorbent was not sufficient for the quantitative removal of copper from wastewater. Fig. 14 illustrates the influence of zeolite (Z1 and Z4) dosage on the adsorption capacity of copper ion. The adsorption capacity

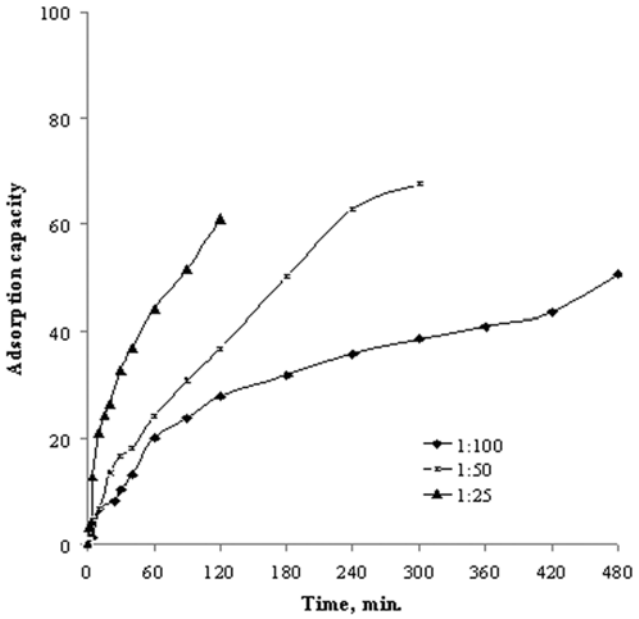


**Fig. 13. Influence of dosage adsorbent on the adsorption process, pH=5.**

was influenced by adsorbent dosage in the case of Z 1 when at 1 : 100 g/100 mL the maximum value was obtained after 300 minutes.

The adsorption capacity was 99.12% when adding 1 : 25 g Z 4/100 mL in the solution, and the removal rate increased with increasing zeolite dosage. The maximum of 99.24% occurred when the maximum zeolite dosage was added into the solution. In this study, because the removal rate was rather high even with the minimum dosage of zeolite, Z4 was added to the solution. Other research [4, 7,28,29] found a similar trend of increasing fly ash dosage resulting in an increasing percentage removal of $Cu^{2+}$.

**4. Adsorption Kinetic Study**

Kinetic models have been used to investigate the mechanism of

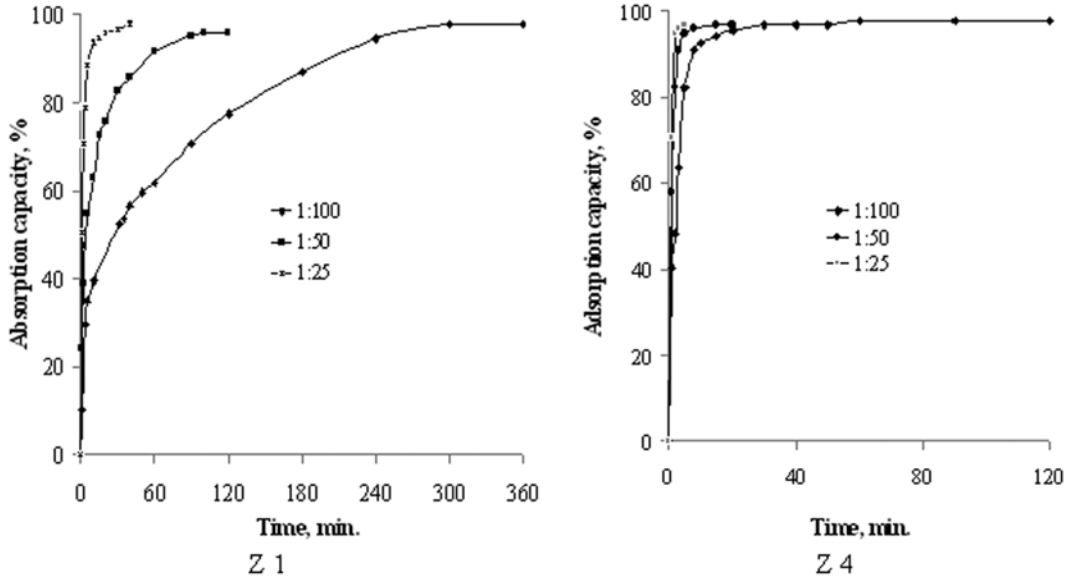


**Fig. 14. Influence of dosage adsorbent on the adsorption process, pH=5.**

adsorption and potential rate controlling steps, which is helpful for selecting optimum operating conditions for the full-scale batch process [30] Pseudo-first-order, pseudo-second-order, Bangham and intraparticle diffusion kinetic models were used.

4-1. Pseudo-first-order Model

The metal uptake q (mg/g adsorbent) was determined as follows:

$$q_e = \frac{(C_0 - C_t)V}{m_s} \quad (2)$$

where $C_0$ and $C_t$ are the initial and metal ion concentrations at moment t (mg/L), respectively, V is the volume of solution (mL), and $m_s$ is the adsorbent weight (g) in dry form.

The pseudo-first-order rate expression based on solid capacity is generally expressed as follows:

$$\frac{dq}{dt} = k_{1,ad}(q_e - q) \quad (3)$$

where, $q_e$ is the amount of $Cu^{2+}$ adsorbed at equilibrium (mg/g), q is the amount adsorbed at time t (mg/g), and $k_{1,ad}$ is the rate constant of first order adsorption (L/min). After integration and applying boundary conditions of t=0 to t and q=0 to $q_e$; the integrated form of Eq. (3) becomes:

$$\log(q_e - q) = \log q_e - \frac{k_{1,ad}}{2.303}t \quad (4)$$

Values of the adsorption rate constant ($k_{1,ad}$) for the copper(II) adsorption onto ash and zeolite were determined from the straight line plot of $\log(q_e - q)$ against t. The data was fitted with a poor correlation coefficient, indicating that the rate of removal of copper onto ash and zeolite does not follow the pseudo-first-order equation.

4-2. Pseudo-second-order Model

The pseudo-second-order equation is also based on the sorption capacity of the solid phase. It predicts the behavior over the whole range of data. Furthermore, it is in agreement with chemisorptions being the rate controlling step and is expressed as [29]:

$$\frac{dq}{dt} = k_{2,ad}(q_e - q)^2 \quad (5)$$

where $k_{2,ad}$ is the rate constant of second-order adsorption (g/mg·min). For the same boundary conditions the integrated form of Eq. (5) becomes:

$$\frac{t}{q} = \frac{1}{k_{2,ad}q_e^2} + \frac{1}{q_e}t \quad (6)$$

This model is based on the assumption that the rate limiting step may be a chemical adsorption involving the valence forces through

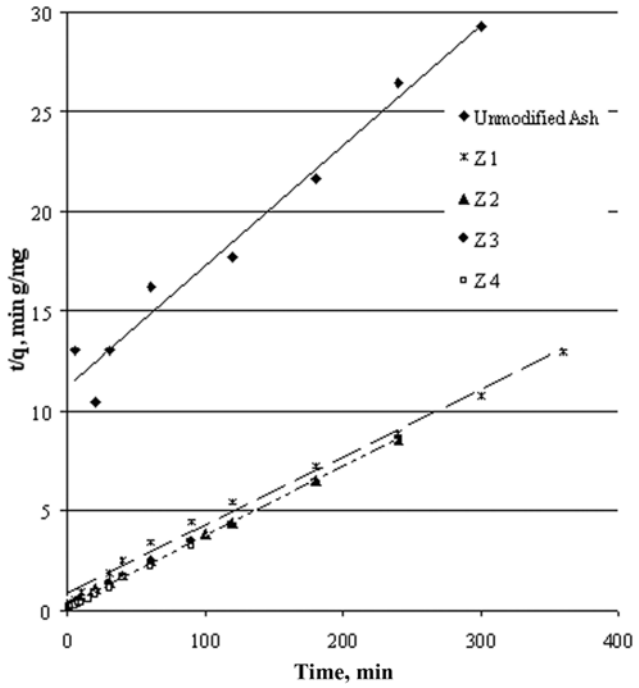


**Fig. 15. Plots of the pseudo-second-order kinetics for the adsorptions of $Cu^{2+}$ on adsorbents, pH=5, 1 : 100, 300 mg/L.**

**Table 2. Kinetic parameters for different adsorbents**

| Adsorbent | Pseudo-second order | | | | Pseudo-first order | Interparticle diffusion |
|---|---|---|---|---|---|---|
| | s/L | $R^2$ | $q_e$, mg/g | $k_2$ | $R^2$ | $R^2$ |
| Ash | 1 : 100 | 0.985 | 14.464 | 0.0005 | 0.9149 | 0.336 |
| | 1 : 50 | 0.939 | 9.664 | 0.0008 | 0.838 | 3125 |
| | 1 : 25 | 0.989 | 4.176 | 0.0091 | 0.8754 | 0.9936 |
| Z1 | 1 : 100 | 0.989 | 27.904 | 0.0017 | 0.9645 | 9121 |
| | 1 : 50 | 0.998 | 13.632 | 0.0168 | 9541 | 0.8271 |
| | 1 : 25 | 0.999 | 6.976 | 0.2096 | 0.8577 | 0.6342 |
| Z2 | 1 : 100 | 0.998 | 27.904 | 0.0051 | 0.9644 | 0.7885 |
| | 1 : 50 | 0.999 | 14.112 | 0.03 | 0.9582 | 0.7623 |
| | 1 : 25 | 0.999 | 7.056 | 0.291 | 0.8362 | 0.5901 |
| Z3 | 1 : 100 | 0.999 | 27.776 | 0.0064 | 0.9438 | 0.7526 |
| | 1 : 50 | 0.995 | 13.792 | 0.0796 | 0.9782 | 0.7978 |
| | 1 : 25 | 0.997 | 6.896 | 0.6007 | 0.8853 | 0.7279 |
| Z4 | 1 : 100 | 0.999 | 27.904 | 0.0356 | 0.8945 | 0.5378 |
| | 1 : 50 | 0.999 | 13.972 | 0.2328 | 0.9161 | 0.6014 |
| | 1 : 25 | 0.993 | 6.896 | 0.9142 | 0.9594 | 0.8641 |

sharing or exchange of electrons between the adsorbent and the adsorbate [10,31]. The model is mentioned in literature for $Cu^{2+}$ adsorption on zeolites [32].

Another possible kinetic model that can be applied in the adsorption processes on porous materials is the interparticle diffusion model. In this case, the amount of heavy metals ions adsorbed can be calculated with the equation [33,34]:

$$q=k_{id}t^{1/2}+C \quad (7)$$

The kinetic curves of the $Cu^{2+}$ uptake on the adsorbent are presented in Fig. 15, when using 1 g of substrate for 100 mL solution.

The pseudo-first order and interparticle diffusion kinetic cannot describe any of the adsorption processes. For our adsorbents, the predominant mechanism can be described by the pseudo-second order kinetics, Table 2.

Based on these results it may be concluded that modifying the FA surface leads to a surface with a moderate amount of active sites; and that different surface modifications are expected, with larger pore concentration on Z 4. This behavior is the result of the FA initial composition and of the dissolution/reprecipitation processes induced during the modification(s).

Table 2 provides the kinetic parameters for the adsorptions of $Cu^{2+}$ on the five adsorbents at various ratios. For the pseudo-second-order model, the values of $R^2$ were higher, confirming the pseudo-second-order nature of the adsorption of $Cu^{2+}$ on the four adsorbents [7].

For our adsorbents the amount of $Cu^{2+}$ adsorbed at equilibrium was 14.46 mg/g for unmodified ash and about 29 mg/g for synthesized zeolites. In other study for zeolite A, the amount of $Cu^{2+}$ ion adsorbed is 37.99 mg/g and 28.88 mg/g for zeolite X. [4]. Literature reported for fly ash and other modified wastes the adsorption capacity about 14.3-42 mg/g [11].

Adsorbent cost is an important factor and may be helpful in comparing the materials [11]. For some adsorbent the costs (USD $/kg) are [11]: bentonite 0.05, blast furnace slag 0.04, fly ash 0.009, peat 0.018-0.069 and commercial activated carbon 1.37-20. These estimates should be considered as indicative, as the cost of the materials can vary, because it depends on various factors, which include its availability, the processing required, the treatment conditions, lifetime issues etc.

## CONCLUSIONS

Experimental data has shown that the studied ash is an efficient adsorbent for heavy metal in general, and copper ions in particular. The use of the ash for copper adsorption leads to a two-fold benefit: an important source of air, water and soil pollution produced by the ash disposal is eliminated, whereas the ash may be used in water treatment as a low cost material for removal of copper.

By using the ash and modified ash as an adsorbent one may reduce the pollution generated by its presence in the environment and decrease the cost of the adsorption process through replacing the expensive adsorbents with this material. The physico-chemical and technological characterization of ash has shown that the ash has the following as principal elements: Si, O, Al, Ca, Fe, K, Mg and traces. The elements are found as oxides or combinations, a fact confirmed by XRD analysis. The ash contains mainly silicate dioxide, alumina and iron dioxide. XRD shows that the ash contains quartz, illite, kaolinite, mullite, hematite, muscovite, rutile and a glassy phase.

The ash is efficient in the adsorption of copper ions at pH 5, with the process being very fast within the first 30 minutes and reaching 97% after 60 minutes.

In the case of a strong acidic condition, the $H^+$ in the solution could neutralize the basic anhydride on the surface of adsorbent, which would decrease the adsorption ability. On the other hand, under a strong alkaline condition, precipitation could occur, and this may inhibit the adsorption process. The mechanism of adsorption of $Cu^{2+}$ was assumed to be a combination of the adsorption at the surface of the adsorbent together with the precipitation from the solution.

The results obtained in this study demonstrate that ash and modified ash can be used as an excellent adsorbent to remove copper from wastewaters with efficiency of over 90% and low cost. Several parameters were studied and the maximum adsorption was found to occur in the pH range of 4.5-6.0 within 120 min of contact. The adsorption efficiencies increased with increasing contact time and decreased with increase in initial copper concentration.

The equilibrium time of $Cu^{2+}$ onto different adsorbent depends on the type of adsorbent. The results show that 60 min was a sufficient time for copper adsorption onto the zeolite Z4; in the case of Z3 the maximum value for adsorption was after 120 minutes. If the concentration of the NaOH solution was 2 M (Z1 and Z2), the maximum value of adsorption capacity was obtained after 3, respectively 4 hours. The ash has a maximum value of adsorption capacity of about 40% after 6 hours of contact. The increase of quantities of copper ions removes and decreases the contact time for the same adsorption capacity justified why we modified the ash.

For our adsorbents, the predominant mechanism can be described by pseudo-second order kinetics.

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