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COPPER REMOVAL FROM AQUEOUS SOLUTION BY NEW ADSORBENTS

Gabriela BUEMA[1], Sorin Mihai CÎMPEANU[2], Răzvan TEODORESCU[2], Marilena BĂRBUȚA[1], Daniel SUTIMAN[1], Roxana Dana BUCUR[3], Ramona Carla CIOCINTA[3], Maria HARJA[1]

[1]"Gh. Asachi" Technical University of Iasi, 73 Prof. dr. doc. D. Mangeron Street, Romania
[2]University of Agronomic Sciences and Veterinary Medicine of Bucharest, 59 Mărăsti Blvd., District 1, 011464, Bucharest, Romania
[3]"Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine of Iasi, 3 M. Sadoveanu Alley, 700490, Romania

Corresponding author email: buema_gabrielaa@yahoo.com

Abstract

Ash from thermal power plant was used as raw material for new adsorbents synthesis using alkaline attack and ultrasonic methods. In detail, it was mixed with 5M NaOH solution and treated at different contact time. The ash and the adsorbents were characterized by electron microscopy/energy dispersive spectroscopy (SEM/EDS), and Fourier Transform Infrared Spectroscopy (FT-IR). The new materials based on ash were applied as water sorbent to remove copper ions. The determination of copper ions was performed by atomic absorption. The results showed that these types of new adsorbents have a good capacity to remove copper ions from aqueous solution. For all synthesized adsorbents the predominant mechanism can be described by pseudo-second order kinetics. The alkaline attack method seems to be the most effective compared with the ultrasonic method and could present application potential for the copper removal.

Key words: *ash, copper ions, kinetic, removal, synthesis.*

INTRODUCTION

Fly ash is a by-product of coal combustion waste (Harja et al., 2011, 2012a). After burning of coal, in power plants result a large amount of different inorganic residues: fly ash, bottom ash, slag and flue gas desulfurization by-products (Gross et al., 2007; Harja et al., 2011), which have low value for utilization and several environmental problems associated with their disposition. Finding some recovery methods has two benefits: reduce pollution, the waste is currently stored, and on the other hand, the synthesis of new materials, cheaper, with high adsorption capacity.
In the last years, unconventional materials such as: fly ash (Querol et al. 2002), metakaolin (Izidoro et al., 2012), slag and aluminum sludge, municipal solid waste ash (Hernandez-Ramirez and Holmes, 2008), chrysotile and rice husk have been used to synthesize zeolites. Function of synthesized conditions determined type of zeolites: zeolite A, linde type A, sodalite, faujasite etc (Rasouli et al., 2012; Ryu et al., 2006).
Several authors have shown that ash can be converted in new materials based on ash by different methods: direct activation (Criado et al., 2007; Inada et al., 2005; Juan et al., 2007; Adamczyk and Bialecka, 2005; Rios et al., 2009), fusion methods (Miyake et al., 2007; Rios et al., 2009), ultrasonic methods (Park et al., 2001; Andac et al., 2005; Wang et al., 2008), molten salt methods (Park et al., 2000a, 2000b). Therefore, the use of ultrasonic methods offers several advantages, when compared with conventional methods presented in the literature, among which the shorter time required for the synthesis process (Park et al., 2001; Andac et al., 2005). Because heavy metals, such as: lead, chromium, nickel, cadmium, copper, etc., can contaminate water by different processes, some methods were proposed to remove them. The most known method is adsorption process, because can be used many types of adsorbents: ash, carbonates, active carbon, new materials based on ash

(zeolites) (Harja et al. 2012b, 2013; Izidoro et al., 2012; Rosales et al., 2012).
The paper presents results of the investigation of Cu^{2+} solutions (pH 5) with ash and new adsorbents based on ash. Therefore, many studies focused on the synthesis of zeolites from waste rich in silica and alumina (Izidoro et al., 2012).

MATERIALS AND METHODS

In this study were used 2 new adsorbents based on ash obtained by ultrasonic and direct activation treatment at 70^0C, 5M of NaOH, corresponding to a ratio s/L of 1:5.
The chemical characterization has shown that the material composition is based on the following chemical elements: Si, O, Al, Ca, Fe, K, Mg, and traces. The elements are found as oxides or combinations, a fact confirmed by FTIR and XRD analysis.
The type of material results by alkaline attack depending on the conditions of synthesis. The temperature is one important factor that influences the type of material synthesized, while the time of contact is another parameter which has to be taken into consideration.
New materials based on fly ash have been widely used as low cost adsorbents for the removal of pollutants from aqueous solution, such as: cooper, nickel, lead, chromium et al.
The chemical and the mineralogical characterizations are presented in the literature (Harja et al., 2012b, 2013).

Adsorption study

Adsorption isotherms were determined using the batch equilibrium method. The adsorption of Cu (II) was studied after adding 1 g of adsorbent into 100 mL of aqueous solution containing Cu (II) concentration of 300 mg/L, pH of 5 and shaking at 300 rpm for 8 hours at room temperature. At certain time intervals, the samples were collected, filtered and analyzed by atomic absorption. The adsorption uptake was calculated by following relation:

$$q = \frac{(C^0 - C) * V}{m_s}$$

Where c^0 - the initial concentration (mg/L), c- the concentration of solution, at the sampling time (mg/L), V - the volume of solution, L, m_s - amount of adsorbent, g.

RESULTS AND DISCUSSIONS

Influence of contact time and type of adsorbent

The efficiency of the removal of Cu^{2+} on C0, C1 and C2 at pH 5 is presented in Figure 1. According to the results presented in Figure 1, at the initial concentration of copper ions of 300 mg/ L, C1 and C2 have the greatest uptake: 24 (300 minute of contact), respectively 27.77 mg Cu^{2+}/g_{ads} after 180 minutes of contact. The lowest capacity is presented by C0: 14.4 mg Cu^{2+}/g_{ads} after 480 minutes of contact.

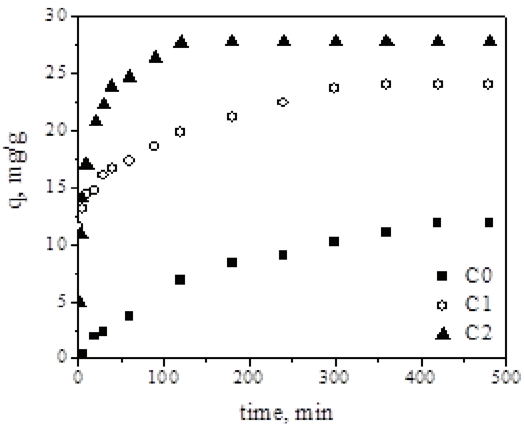


Figure 1. Influence of type of adsorbent at pH 5, Cin=300 mg/L

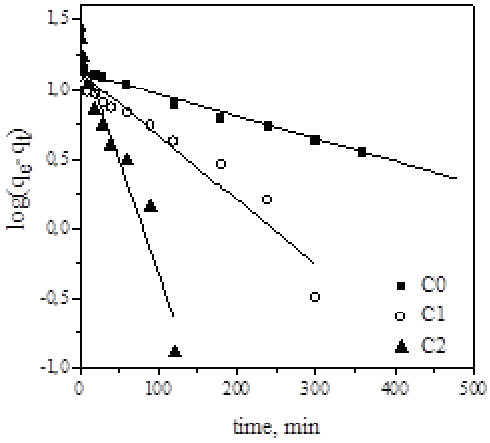
Adsorption kinetics

Several kinetic model equations were proposed for adsorption process, including the pseudo first order, the pseudo second order, diffusion model, and intraparticle diffusion model. The equations are presented in literature (Ahmaruzzaman, 2010). In this study to define the adsorption kinetics of Cu^{2+} onto C0, C1 and C2, the pseudo first order and pseudo second order kinetic parameters of the adsorption process were investigated. The plot of the kinetic models for Cu^{2+} ions onto the adsorbents are shown in Figure 2 and the results of kinetic parameters are given in Table 1.

Table 1. Kinetic parameters

Adsorbent	Pseudo I model	Pseudo II model	
	R^2	R^2	q_e, mg/g
C0	0.914	0.985	14.4
C1	0.919	0.993	24
C2	0.943	0.999	27.776

As seen from Table 1, for all adsorbents the adsorption kinetic is described by the pseudo second order equation.



a

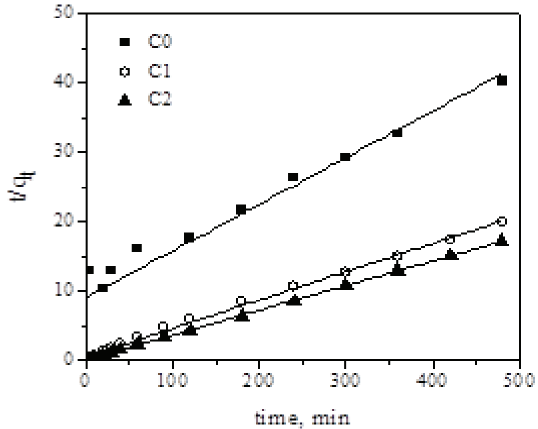


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Figure 2. Adsorption kinetic of Cu2+ ions onto C0, C1 and C2: a-Pseudo first order, b-Pseudo second order

CONCLUSIONS

This study indicated that new adsorbents based on ash could effectively remove copper ions from aqueous solutions. The use of new materials based on 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 adsorbent for removal of copper.

The uptake efficiencies increased with increasing of contact time. The highest adsorption capacity was observed in the case of the adsorbent synthesized by direct activation at ratio 1:5, temperature 70°C, C_{NaOH}=5M (approximately 28 mg Cu^{2+}/g_{ads} after 180 minutes of contact).

For ash and new materials based on ash adsorption kinetic is described by the pseudo second order equation.

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