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The Influence of Clayey Pellet Size on Adsorption Efficiency of Metal Ions Removal from Waste Printing Developer

Kiurski S. Jelena, Ranogajec G. Jonjaua, Oros B. Ivana, Kecić S. Vesna

Abstract**—**The adsorption efficiency of fired clayey pellets of 5 and 8 mm diameter size for Cu(II) and Zn(II) ion removal from a waste printing developer was studied. In order to investigate the influence of contact time, adsorbent mass and pellet size on the adsorption efficiency the batch mode was carried out. Faster uptake of copper ion was obtained with the fired clay pellets of 5 mm diameter size within 30 minutes. The pellets of 8 mm diameter size showed the higher equilibrium time (60 to 75 minutes) for copper and zinc ion. The results pointed out that adsorption efficiency increases with the increase of adsorbent mass. The maximal efficiency is different for Cu(II) and Zn(II) ion due to the pellet size. Therefore, the fired clay pellets of 5 mm diameter size present an effective adsorbent for Cu(II) ion removal (adsorption efficiency is 63.6%), whereas the fired clay pellets of 8 mm diameter size are the best alternative for Zn(II) ion removal (adsorption efficiency is 92.8%) from a waste printing developer.

Keywords**—**Adsorption efficiency, clayey pellet, metal ions, waste printing developer.

I. Introduction

HEAVY metal ions are reported to be priority pollutants due to their toxicity and mobility in natural water ecosystems. They are stable and persistent environmental contaminants since they are neither degraded nor destroyed [1]. Even at low concentrations, metals can be toxic to humans and other biological systems. It is well known that the selective removal of metal ions in dilute solutions is very difficult by conventional wastewater treatment methods. Therefore, it is vital to safeguard public health and security and accomplish environmental integrity through the application of reliable but low-cost treatment techniques [2].

The contamination of the environment from a variety of heavy metal sources has become an increasingly serious problem in recent years. Industrial and municipal waste frequently contain heavy metal ions, such as lead, copper, cadmium, zinc, and nickel, which are amongst the most common pollutants found in industrial effluents [3]–[5].

Printing industry, as a polluter, also generates highly colored wastewaters with significant content of organic and inorganic matters [6]. Heavy metals (chromium, zinc and copper) found in a waste printing developer come from dye residue, and they tend to be accumulated in living organisms, causing numerous diseases and disorders [7]–[15].

Various wastewater treatment techniques, including adsorption, precipitation, ion exchange and reverse osmosis, have been employed to eliminate or reduce toxic heavy metals. Adsorption on solids is the most common used method because it is highly efficient, inexpensive and easy to adapt [15], [16].

The use of clay as an adsorbent to remove pollutants from wastewater has recently attracted increasing attention, because they are readily available, inexpensive and environmental friendly. The wide usefulness of clays is a result of their high specific area, high chemical and mechanical stability, and a variety of surface and structural properties. Because of their particle size, clays can exhibit an array of novel properties that can be used to develop new water treatment technologies and to improve the existing ones. Their chemical nature and pore structure generally determine the adsorption ability [17]. These characteristics make them good cation adsorbents with large specific surface areas for ion exchange or electrostatic attraction [18]. Thus clay material can be a promising adsorbent for environmental purification purposes.

The removal of heavy metals using different types of clay has been the subject of several recent studies [19]–[25].

Our previous work was undertaken to design a low-cost and effective fired clay pellets as well as to apply them in real batch adsorption experiments [17]. The objective of this study was to investigate the adsorption efficiency of the fired clay pellet size for Cu(II) and Zn(II) ion removal from a waste printing developer.

II. Materials And Methods

A. Materials

The sample of waste printing developer was taken from an offset printing facility, Novi Sad (Serbia).

Fired clay pellets, diameter size of 5 mm - FCP5 and 8 mm - FCP8, were chosen for the batch adsorption experiments. The raw clayey mixture consisted of natural pozzolanic

J. Kiurski is from the University of Novi Sad, Faculty of Technical Sciences, Department of Graphic Engineering and Design, Trg Dositeja Obradovića 6, 21000 Novi Sad, Serbia (phone: +381 21 4852623; fax: +381 21 458133; e-mail: kiurski@uns.ac.rs).

J. Ranogajec is from the University of Novi Sad, Faculty of Technology, Department of Materials Engineering, Bul. Cara Lazara 1, Novi Sad, Serbia (phone: +381 21 4853757; fax: +381 21 450413; e-mail: janjar@uns.ac.rs).

I. Oros is from the University of Novi Sad, Faculty of Technical Sciences, Department of Graphic Engineering and Design, Trg Dositeja Obradovića 6, 21000 Novi Sad, Serbia (phone: +381 21 4852554; e-mail: icki@uns.ac.rs).

V. Kecić is from the University of Novi Sad, Faculty of Technical Sciences, Department of Graphic Engineering and Design, Trg Dositeja Obradovića 6, 21000 Novi Sad, Serbia (phone: +381 21 4852554; e-mail: kecic@uns.ac.rs).

material, waste glass, surfactant and wooden dust. The clayey material was shaped by extrusion, dried at 105 °C during 24h and fired at 1020°C in laboratory conditions [23]. The chemical composition of the the natural pozzolanic material and the waste glass components (Table I) present a good source of SiO_2 and Al_2O_3 necessary for the glassy structure formation during the sintering process. The presence of Na_2O in WG (11.05 mass %) presented an important compound which had an important influence on the decrease of the sintering temperature of the raw material [17].

TABLE I
CHEMICAL COMPOSITION OF THE NATURAL POZZOLANIC MATERIAL AND THE WASTE GLASS [17]

Oxides	Natural pozzolanic material	Waste glass
SiO_2	76.60	72.23
Al_2O_3	5.08	0.61
Fe_2O_3	2.32	1.84
CaO	0.67	6.28
MgO	1.98	4.32
K_2O	1.20	0.36
Na_2O	2.10	11.05
Loss of ignition	10.10	/

All used chemicals were of analytical reagent grade (Merck, Germany). In order to obtain real concentrations of Cu(II) and Zn(II) ion, present in a waste printing developer, the solutions with 3.059 mg/L Cu(II) ion concentration and 17.302 mg/L Zn(II) ion concentration were prepared.

B. Methods

The adsorption of Zn(II) and Cu(II) ion onto fired clay pellets, diameter size of 5 mm and 8 mm, was studied in laboratory batch mode. The equilibrium time experiments were carried out by shaking 0.2 g of each adsorbent with 25 mL of aqueous working solution of Zn(II) ion (17.302 mg/L) and Cu(II) ion (3.059 mg/L) at shaking speed of 160 rpm, and shaking times of 15, 30, 45, 60, 75, 90, 105 and 120 min. At the end of the predetermined time intervals, the solutions are centrifuged for 10 minutes at 3000 rpm and then filtered through a quantitative filter paper (Advantec, grade 5C). The equilibrated Zn(II) and Cu(II) ion concentrations were determined in the acidified filtrate (cc HNO3) by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) method using a PerkinElmer Elan 5000 mass spectrometer [17].

The adsorption experiments were performed by shaking the different amounts of adsorbent (0.04 - 0.24 g) with 25 mL of a waste printing developer. The other parameters were constant: ambient temperature (23.4°C), pH value (13.0) and shaking speed (160 rpm).

III. RESULTS AND DISCUSSION

In our previous experiments, it was found that the fired clay pellets can serve as a good low-cost adsorbent for the removal of zinc ion from a waste offset developer [15], [23], [26], [27]. Therefore, the examination by a moderate influence of the pellet of different sizes on the adsorption efficiency of removing zinc and copper ion is performed.

Contact time is an important parameter because it determines the adsorption kinetics of an adsorbent at a given initial concentration of the adsorbate [15]. The influence of contact time on Cu(II) and Zn(II) ion adsorption was investigated for 120 minutes, Figs. 1 and 2.

Clayey pellets, diameter of 5 mm, FCP5, showed a faster uptake of Cu(II) ion with equilibrium established within 30 minutes than FCP8 (whose optimal time 75 minutes), Fig. 1. The optimal contact time for Zn(II) ion adsorption was 60 and 75 minutes for FCP8 and FCP5, respectively, Fig. 2. The reason for the rapid initial uptake of both Cu(II) and Zn(II) ion is the presence of active sites on the clayey surface that gradually became occupied.

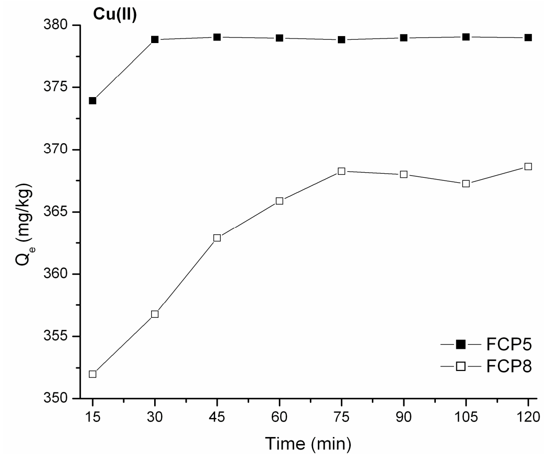

Fig. 1 Influence of the contact time on Cu(II) ion adsorption

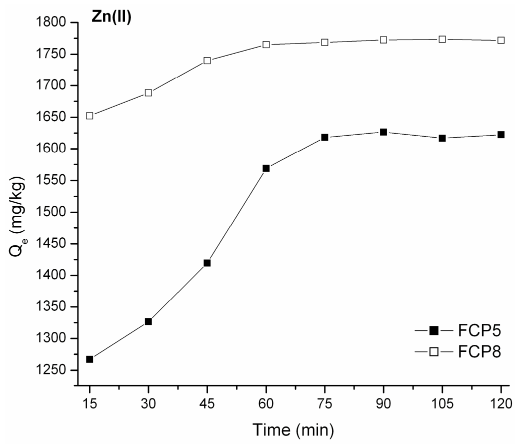

Fig. 2 Influence of the contact time on Zn(II) ion adsorption

Also, the pore-size distribution analysis of the fired clay pellets indicated the presence of a significant amount of large pores in the range from 16 - 32 µm in the case of the FCP5, while the FCP8 possessed a much higher amount (approximately 70%) of the pores in the range from 2 to 4 µm, Fig. 3 [17]. The existing pore size distribution of the FCP5 clayey particles caused higher water absorption and lower compressive strength values causing smaller pellets adsorbed the copper faster than zinc ion.

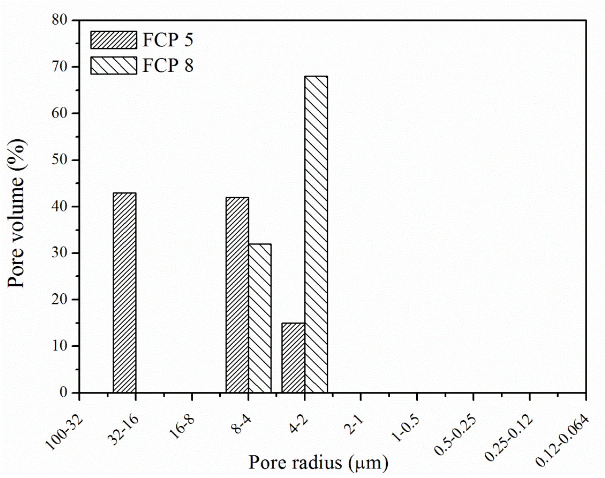

Fig. 3 Pore size distribution of the fired clayey pellets [17]

The distribution of metal ions between the fired clay pellets and the waste printing developer is important for the determination of the efficiency and capacity of the adsorbents. Distribution coefficient, K_d, is a measure of sorption of Cu(II) and Zn (II) ion onto the fired clay pellets and it is defined as the ratio of adsorbed adsorbate (metal ions) per unit mass of the adsorbents (fired clay pellets). The values of distribution coefficients, K_d, for Cu(II) ion varied from 181.6 to 822.9 L/kg and from 153.2 to 623.8 L/kg using FCP5 and FCP8 as the adsorbents. Whereas, the application of FCP5 and FCP8 showed a wider range of distribution coefficients for Zn(II) ion: 1020.2 to 4425.8 L/kg and 1348.1 to 5111.7 L/kg, respectively.

Considering the obtained K_d values and the influence of the pellets size, the following decreased order was obtained for copper ion: FCP5 > FCP8. The coefficient of distribution for zinc ion showed the opposite order: FCP8 > FCP5.

The influence of adsorbent mass on adsorption efficiency of Cu(II) and Zn(II) ion removal is presented in Figs. 4 and 5. It was observed that the adsorption efficiency of Cu(II) and Zn(II) ion increased with the increase of the adsorbent amount. The reason is the increase of the surface negative charge, decrease of the electrostatic potential near the solid surface, favors adsorbent-adsorbate interactions as well as the availability of more active sites on the clay surface [9]. The maximum adsorption efficiency of 63.6% for Cu(II) ion removal was achieved with FCP5, Fig. 4, but the fired clay pellets of 8 mm diameter size, FCP8, had the highest effectiveness for Zn(II) ion removal (92.8%), Fig. 5. The obtained order of distribution coefficients is followed by the adsorption efficiencies for both metal ions.

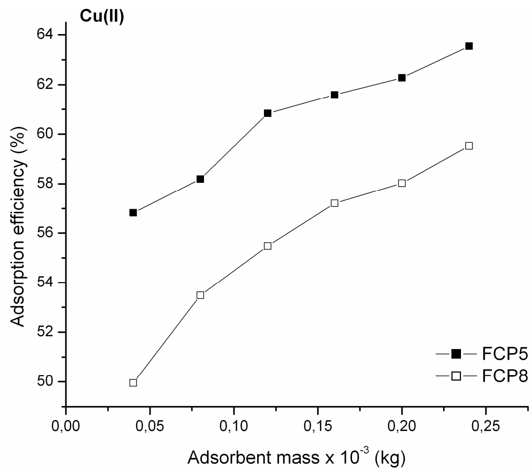

Fig. 4 Influence of adsorbent mass on adsorption efficiency of Cu (II) ion

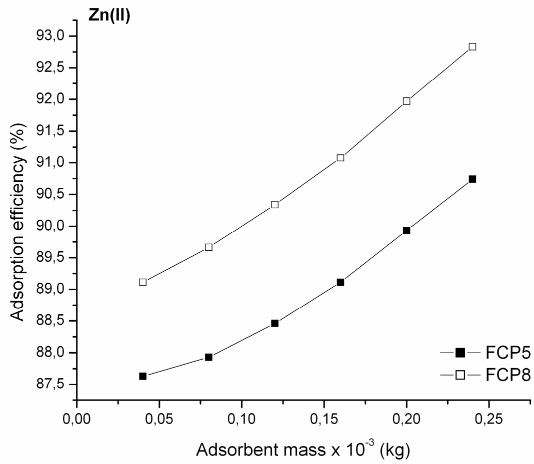

Fig. 5 Influence of adsorbent mass on adsorption efficiency of Zn (II) ion

IV. Conclusions

The adsorption efficiency of the fired clayey pellets were tested in laboratory batch mode in order to remove undesired Cu(II) and Zn(II) ion from a waste printing developer. The influence of pellets size on distribution coefficients showed the following decreased order: for copper ion it was FCP5 > FCP8 and for zinc ion it was FCP8 > FCP5. The obtained order of distribution coefficients is followed by the adsorption efficiencies for both metal ions.

Fired clay pellets of 5 mm diameter size showed the maximum adsorption efficiency of 63.6% for Cu(II) ion removal, while the removal of Zn(II) ion was highly effective (92.8%) with the fired clay pellets of 8 mm diameter size.

Therefore, the used clayey pellets could be a good alternative adsorbents for Cu(II) and Zn(II) ion removal from a waste printing developer.

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