

The Purification of Waste Printing Developer with the Fixed Bed Adsorption Column

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Abstract—The present study investigates the effectiveness of newly designed clayey pellets (fired clay pellets diameter sizes of 5 and 8 mm, and unfired clay pellets with the diameter size of 15 mm) as the beds in the column adsorption process. The adsorption experiments in the batch mode were performed before the column experiment with the purpose to determine the order of adsorbent package in the column which was to be designed in the investigation. The column experiment was performed by using a known mass of the clayey beds and the volume of the waste printing developer, which was purified. The column was filled in the following order: fired clay pellets of the diameter size of 5 mm, fired clay pellets of the diameter size of 8 mm, and unfired clay pellets of the diameter size of 15 mm. The selected order of the adsorbents showed a high removal efficiency for zinc (97.8%) and copper (81.5%) ions. These efficiencies were better than those in the case of the already existing mode adsorption. The obtained experimental data present a good basis for the selection of an appropriate column fill, but further testing is necessary in order to obtain more accurate results.

Keywords—Clay materials, fix bed adsorption column, metal ions, printing developer.

I. INTRODUCTION

COPPER and zinc are among the most common heavy metals in printing wastewaters. Apart from being hazardous for living organisms when the specific quantity limits are exceeded, both metals accumulate in nature as they cannot be biodegraded [1], [2]. While the accumulation of Cu(II) ion in human body causes brain, skin, pancreas and heart diseases, Zn(II) ion, which is on the list of priority pollutants proposed by Environmental Protection Agency (EPA), causes serious poisoning. Also, the Agency for Toxic Substances and Disease Registry of the U.S. Department of Health and Human Services has designated copper and zinc as priority pollutants due to their toxicity [1]–[5].

A number of technologies, such as coagulation/flocculation, membrane filtration, adsorption, reverse osmosis, ion exchange and solvent extraction, have been developed over the years to remove heavy metals from industrial wastewaters

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[4]. Besides the batch technique, adsorption process in a fixed bed column has also become frequently used in many pollution control processes by application of various low-cost adsorbents (clay, bentonite, and zeolite) [6].

In recent years, there has been more and more focus on the testing of different clay minerals in the purification of waste flows [7]–[9]. The main advantages of clay minerals, such as high ion sorption/exchange capacity, low permeability, swelling ability, chemical and mechanical stability, and large specific surface area, make clays promising alternative adsorbents for the removal of metal ions [10], [11].

Our previous adsorption experiments in batch mode confirmed that the fired and unfired clayey pellets with various diameter sizes can serve as good low-cost adsorbents for the metal ions removal from a waste offset printing developer [12]–[14]. Therefore, the aim of the present study was to test the potential of the newly designed clayey pellets as the beds in the column adsorption process.

II. MATERIALS AND METHODS

A. Adsorbate and Adsorbent

1. Adsorbate

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

2. Adsorbent

Fired (diameter sizes of 5 mm – FCP5 and 8 mm – FCP8) and unfired (diameter size of 15 mm – UFCP15) clayey pellets were chosen as the adsorbents. The raw clayey mixture based on natural pozzolanic material, waste glass, suitable surface active material and wooden dust was shaped by extrusion, then dried (105°C, 24h) and fired at 1020°C in laboratory conditions [15].

B. Characterization of Material

The chemical composition of the pozzolanic material and waste glass was obtained by using the standard alkali-silicate chemical analysis. The textural properties of the clayey pellets were examined by mercury porosimetry [16].

C. Adsorption Method

1. Laboratory Batch Mode

The adsorption of Zn(II) and Cu(II) ions onto clayey pellets, FCP5, FCP8 and UFCP15, was studied in laboratory batch mode.

The equilibrium time experiments were carried out by shaking a known mass of each adsorbent (0.2 g) with 25 mL of aqueous working solutions of Zn(II) (17.302 mg/L) and Cu(II) (3.059 mg/L) ions with a shaking speed of 160 rpm, and shaking times of 15 to 120 min, with an interval of 15 min. At the end of the predetermined time intervals, the solutions were 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) ions 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 [14], [15].

The adsorption experiments were performed by shaking the different mass of adsorbents (0.04 - 0.24 g) with 25 mL of the used waste printing developer. The obtained system was shaken for 75/60/30 min (the optimal contact time for defined adsorbent) in order to reach the adsorption equilibrium. At the end of the optimal contact time, the residual concentrations of Zn(II) and Cu(II) ions were determined by ICP-MS method.

2. Column Experiments

The column experiments were conducted by using a glass column filled with clayey pellets (FCP5, FCP8 and UFCP15), activated carbon (AC), glass pearls. The glass column had an inner diameter of 18 mm and a height of 300 mm. The known mass of each clayey bed (2 g) was placed into the column yielding the total bed height of 100 mm, Fig. 1.



Fig. 1 Column filled with the adsorbents

The adsorbents were packed according to the optimal contact time for defined adsorbents in the batch mode. The quantity of 20 mL of the waste printing developer, with the known initial concentrations of metal ions (Zn(II) - 17.302 mg/L and Cu(II) - 3.059 mg/L), was passed through the newly designed column. At the end of the experiment, the concentration of the investigated metal ions was analyzed by ICP-MS method.

III. RESULTS AND DISCUSSION

A. Characterization of the Clayey Pellets

The chemical composition of the used pozzolanic material and the waste glass present a good source of SiO₂ and Al₂O₃

necessary for the glassy structure formation during the sintering process, Table I. The quantity of Na₂O in the waste glass (11.05 mass %) presented an important compound which had significant influence on the sintering temperature decrease of the raw material composition [15].

TABLE I
 CHEMICAL COMPOSITION OF THE NATURAL POZZOLANIC MATERIAL AND WASTE GLASS [14]

Oxides	Natural pozzolanic material	Waste glass
SiO ₂	76.60	72.23
Al ₂ O ₃	5.08	0.61
Fe ₂ O ₃	2.32	1.84
CaO	0.67	6.28
MgO	1.98	4.32
K ₂ O	1.20	0.36
Na ₂ O	2.10	11.05
Loss of ignition	10.10	/

The results of pore-size distribution analysis, Fig. 2, indicated the presence of a significant amount of large pores (pore radius in the range of 2 - 8 μm) in the case of the pellets FCP8.

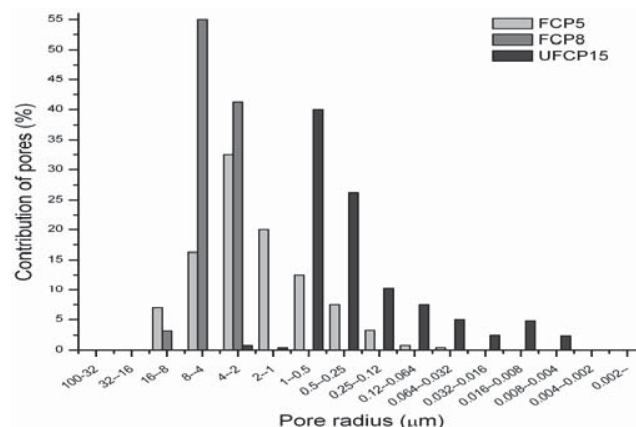


Fig. 2 Pore size distribution of the clayey pellets

The FCP5 pellets showed the largest amount of small pores (pore radius in the range 1 - 4 μm). On the other hand, the UFCP15 pellets can be characterized by larger amount of small pores (0.25 to 1 μm). Also, the UFCP15 pellets possess higher specific surface area and porosity (4.51 m²/g and 29.75%) compared with the FCP5 (0.41 m²/g and 18.08%) and the FCP8 (0.31 m²/g and 14.05%). The existing pore size distribution of the designed clayey particles affected the higher water absorption and lower compressive strength values [15].

B. The Effect of Contact Time on the Adsorption Process

The adsorption phenomenon of zinc and copper ions on the defined fired and unfired clayey pellets can be interpreted in terms of the contact time. The contact time for Zn ions is ranging from 30 to 75 minutes for different sizes of the clay pellets. After 30, 60 and 75 minutes (contact time for UFCP15, FCP8 and FCP5 pellets, respectively), there was no

significant increase in the uptake capacity for zinc ion removal suggesting that the equilibrium had been established.

The optimal contact time for copper ion removal with the FCP5 and FCP8 adsorbents was 30 and 75 minutes, respectively. The UFCP15, after 30 minutes of shaking, showed the same trend as the equilibrium established with Zn ions. The fast rate of adsorption observed at the initial stage can be explained by an availability of more active sites on the clayey surface. It was also affected by the increase in surface negative charge and decrease in the electrostatic potential near the clayey surface [12]–[16].

In the initial stage of the column experiments, the following decreased order of the contact time for zinc ions removal was obtained: UFCP15 > FCP8 > FCP5.

C. The Effect of Adsorbent Mass on the Adsorption Process

The effect of the pellets mass on the adsorption efficiency in the designed batch mode was represented in Figs. 3 and 4.

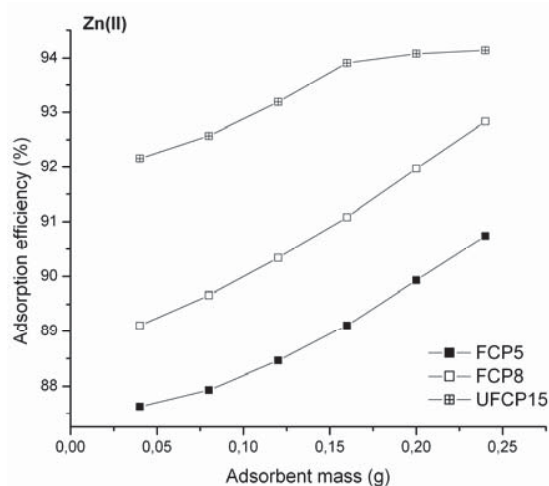


Fig. 3 The effect of pellets mass on the adsorption efficiency of Zn ions

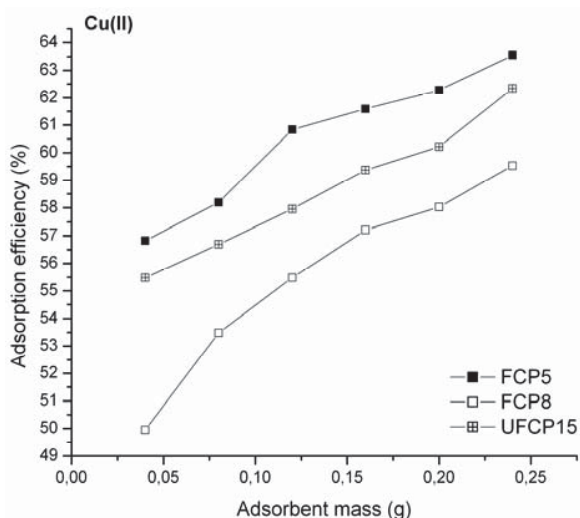


Fig. 4 The effect of pellets mass on the adsorption efficiency of Zn Cu (b) ions

Evidently, the removal of zinc and copper ions from the waste printing developer increased with the increase of the adsorbent mass.

The maximum adsorption efficiency of 94.1% was obtained for the removal of zinc ions with the UFCP15 pellets (Fig. 3). The FCP5 pellets showed the highest adsorption efficiency (63.6%) for copper ion removal, Fig. 4. Precisely, the highest surface functionality (4.51 m²/g) and porosity (29.75%) and the presence of the largest amounts of small pores (pore radius in the range 0.25 - 1 μm) in the case of the UFCP15 pellets confirm the availability of more active sites for the interaction with the zinc ions.

Considering the adsorption efficiencies of the used adsorbents, the following decreased orders were obtained: UFCP15 > FCP8 > FCP5 (zinc ion removal) and FCP5 > UFCP15 > FCP8 (copper ion removal). The obtained trend of adsorption efficiency for both metal ions in the batch mode was in accordance with the optimal contact time. By analyzing the results of adsorption in the batch mode, it was concluded that the column fill may depend on the efficiency of the individual adsorbents or on the pellet size.

The results of adsorption efficiency in the fixed bed column experiments showed higher removal efficiency for zinc (97.8%) and copper (81.5%) ions than in the batch mode. In order to get the most precise results regarding copper ion removal from a waste printing developer in the future column experiments, it is important to follow the contact time orders.

IV. CONCLUSION

The fired and unfired clayey pellets, as the beds in the column adsorption process, were tested in order to remove zinc and copper ions from a waste printing developer. The order of adsorbent package in the column was obtained based on the adsorption results in a batch mode. The adsorbents, in form of pellets, were packed in the following order: FCP5, FCP8, UFCP15.

Considering the adsorption efficiencies of the used adsorbents in the batch mode, the following decreased orders were obtained for zinc ion removal: UFCP15 > FCP8 > FCP5 and FCP5 > UFCP15 > FCP8 for copper ion removal.

Certainly, the fixed bed column experiments showed the highest adsorption efficiencies of zinc (97.8%) and copper (81.5%) ions removal in relation to the batch mode.

As the performing tests present a good basis for the selection of a proper column fill, an additional detailed investigation has to be performed in the future, in order to obtain the most precise results regarding adsorption efficiency.

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