Unfired Clayey Pellets as the Adsorbents for Metal Ions Removal from a Waste Printing Developer

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Abstract
The paper analyses the application of various forms of unfired clay pellets (whole and half), for the removal of zinc and copper ions from a waste printing developer. The adsorption experiments were performed in batch mode. The textural properties of defined clayey pellets were examined by mercury porosimetry.
Textural characterization showed a significant amount of the small pores in the case of whole pellets in relation to half pellets. The efficiency of the metal ions removal significantly increases with the increase of the adsorbents mass. The removal efficiency varied between 50 and 94%. Considering the adsorption efficiencies, the following order of unfired clay pellets was noticed: whole pellet > half-pellet. The ionic radius of metal ions and the obtained trends of adsorption efficiency show that the selectivity sequence of metal ions on the unfired clay pellets was Zn > Cu.
Therefore, the unfired clayey adsorbents present the promising alternatives for purification of waste printing developers.

Introduction
Industrial wastewaters are often characterized by considerable heavy metal content and, therefore, it is required to treat them prior disposal into water. The heavy metals, such as lead, copper, cadmium, zinc, silver and nickel are the most common pollutants found in industrial and printing effluents [1, 2]. Adsorption with the clayey minerals is the low-cost promising alternatives for the treatment of heavy metals present in wastewater. There are many advantages of using clay as an adsorbent: cost of clay is relatively low compared to other alternative adsorbents; clay minerals have high specific surface area, excellent physical and chemical stability and other structural and surface properties [3]. Thus, clays can adsorb all kinds of pollutants from large volumes of aqueous solutions. Also, clays are used as barriers to prevent contamination of the subsoil and groundwater by the leaching of landfill containing metals [3, 4].
The aim of this research was to evaluate the adsorption efficiency of different forms of unfired clay pellets for waste printing developer purification.

Materials and methods
Printing developer. The sample of waste printing developer was taken from an offset printing facility in Novi Sad (Serbia).
Clayey pellets. The newly designed unfired clayey pellets (whole and half) of diameter size 15 mm were chosen as the adsorbents. The raw clayey mixture consists of natural pozzolanic material, waste glass, surfactant and wooden dust. The material was shaped by extrusion and dried at 105 °C during 24h in laboratory conditions [5].
The textural properties of the unfired clayey pellets were examined by mercury porosimetry [6].

Methods. The adsorption experiments were performed in batch mode at standard procedure [6]. In order to reach the adsorption equilibrium waste printing developer were shaken for 30 min (the optimal contact time for defined adsorbent) [7]. The residual concentrations of Zn(II) and Cu(II) ions were determined by Inductively Coupled Plasma Mass Spectrometry method using a PerkinElmer Elan 5000 mass spectrometer.

Results and discussion

Characterization of the unfired clay pellets

The investigation of textural properties by mercury injection is very suitable for the characterization of porous structures in the range of the pore radius of 0.05 µm. The results of textural characteristics are shown in Figure 1 and Table 1. Based on the obtained results it was observed a monomodal pore radius distribution of the investigated adsorbents, Figure 1.

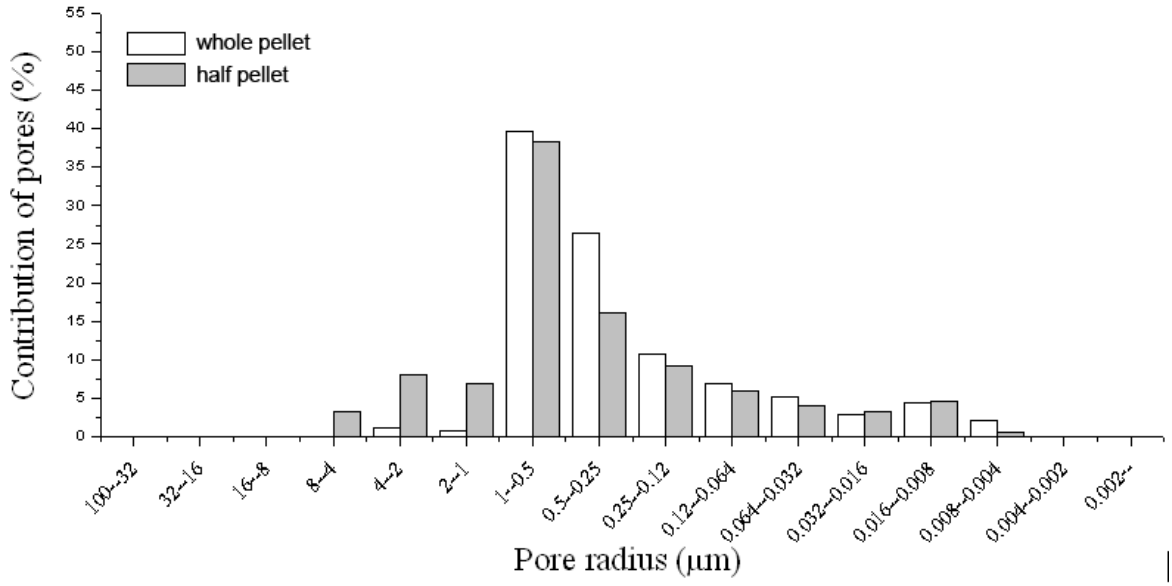


Figure 1. Pore size distribution of the unfired clayey pellets

The pore size distribution analysis of the unfired clay pellets (whole and half) indicates the presence of a significant amount of the large pores (pore radius above 1 µm) in the case of half pellets in relation to whole pellets. Whole pellets are characterized by a slightly larger amount of small pores less than 1 µm, Figure 1. Also, whole pellets showed a higher specific surface area (4.51 m^2/g) in relation to half pellets, Table 1.

Table 1. The results of specific surface area

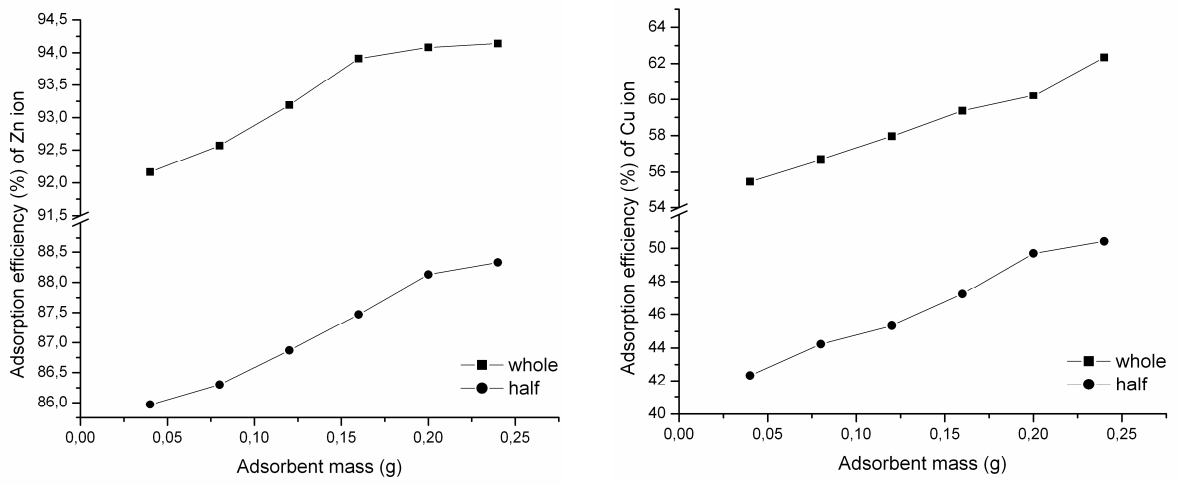
Unfired clay pellet	Specific surface area (m^2/g)
whole	4.51
half	3.85

Adsorption efficiency

The increase of the metal ion adsorption with the usage of clayey materials can be attributed to the increased surface area and the availability of more adsorption sites [8]. Also, the chemical and mechanical stability allow their application in various states and improve the consistency of adsorption relative to less stable materials [8-10].

The influence of unfired pellets forms on the adsorption efficiency, Figure 2a and 2b, indicates that the removal of zinc and copper ions from a waste printing developer increases

with the increase of the adsorbent mass. The maximum adsorption efficiencies of the zinc ion removal by using whole and half pellets were 94.1 and 88.3%, respectively (Figure 2a). Whole and half pellets showed the lower adsorption efficiency (62.4 and 50.4%, respectively) for copper ion removal, Figure 2b. Considering the adsorption efficiencies of used adsorbents the following decrease order was obtained: whole pellet > half pellet.
As whole pellets show a higher surface functionality (specific surface area 4.51 m^2/g, Table 1) a great number of sites is available for the interaction with zinc and copper ion present in a waste printing developer. Beside the availability of the surface sites, the observed trend of adsorption efficiency can also be related to the pore size distribution of whole pellets, Figure 1.



a) b)

Figure 2. Efficiency of zinc (a) and copper (b) ions removal using unfired clay pellets

The trends of adsorption efficiency can also be explained based on the ionic radius of metal ions. The smaller ionic radius of a metal ion means the higher adsorption rate [11]. As Zn(II) and Cu(II) ions have approximately the same ionic radius it is expected the same removal efficiency. Our study shows that the selectivity sequence of metal ions on the unfired clay pellets is Zn > Cu.

Conclusions

The adsorption efficiency of the unfired clay pellets (whole and half) was tested in order to remove zinc and copper ions from a waste printing developer. The presence of a significant amount of the small pores (pore radius less than 1 μm) was observed in the case of whole pellets in relation to half pellets. The maximum adsorption efficiencies of zinc (94%) and copper (62%) ions removal were achieved by using whole pellets. Considering the adsorption efficiencies of used adsorbents the following decrease order was obtained: whole pellet > half pellet. Based on the obtained adsorption efficiency the selectivity sequence of metal ions on the unfired clay pellets was Zn > Cu.

Acknowledgements

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