

STUDY OF ADSORBENTS FROM UKRAINIAN KAOLINITE CLAY FOR THE REMOVAL OF NICKEL: INSIGHT AND PRACTICAL APPLICATION FOR WATER TREATMENT

Currently, the mining sector is facing increasing pressure to implement the principles of sustainable mining [1]. Mining provides also economic and social development, employment, supply of basic raw materials to the society, and supports economic, social and infrastructural development in underdeveloped countries and areas [2,3].

Among common purification techniques, adsorption has lately gained much attention because it is an eco-friendly, cost-effective, and simple operating technology. In recent years, much attention has been focused on the selection and/or production of low-cost adsorbents with good metal-binding capacities [4]. Many investigations in this field indicated zeolite as a cost-effective adsorbent because of its good metal binding capacity, local availability in large quantities, simple operating technology, and general lack of secondary pollution [5] presented experimental data on the removal of ammonia by zeolite. The main disadvantage of using zeolites for such needs in Ukraine is their remote geographical location from the studied accumulation lakes and old river beds [6]. In [7] the adsorption properties of heavy metals (HM) by various volcanic tuffs and kaolins, and the dependence of their adsorption capacity on pH, temperature, initial concentration of HM were studied.

Kaolins represent clays that are very common in Ukraine. Their value is determined by the peculiarity of physicochemical properties and the scale of their use in almost all industries.

There are numerous scientific reports on the experimental studies of HM adsorption by kaolins, performed in acidic and weakly alkaline waters [7–9]. One of the important factors that may influence HM adsorption by kaolin is total water mineralization. There is a lack of precise data on the relationship between the HM sorption capacity in acidic and weakly alkaline water with different TDS values and the mineral composition of kaolins.

Taking the above issues into account, this research was focused on determining the mineralogical composition of red and white kaolins from one quarry. Based on the obtained results, it was essential to test the relationship between their sorption capacity in acidic water and weakly alkaline water (with different TDS values) and determine its dependence on the mineralogical composition.

The study also aimed at assessing the influence of doses of red and white kaolins on the sorption process efficiency. This is indispensable in determining the economic effect of their application. To ensure the ecological and economic effect of using the kaolins from Ukraine it was essential to search for accumulation lakes of mine waters located in the close vicinity of kaolin quarries.

The presented research should allow for the development of an effective technological key for the reclamation of water reservoirs in mines in the Krivbas Basin with the use of red kaolins, previously treated as industrial waste and subjected to landfilling.

This study is focused on the impact of kaolin mineralogy, kaolin doses, and water total dissolved solids on the adsorption capacity of Ni^{2+} . It is concentrated on analysing the influence of kaolin mineralogy and doses on the adsorption capacity of Ni^{2+} in acidic and alkaline water (at different mineralization values).

Material used in the study was sampled from the Murzyntski kaolin deposit located in central Ukraine (49°08'10.0"N 30°55'16.0"E). Two samples of loose kaolin samples, with a mass of 0.5 kg each were taken for the examination; they represented the red (sample R-K) and white (sample W-K) kaolin raw material which was macroscopically distinguishable in the mine excavation (Figure 1).



Figure 1. Kaolin samples from the Murzyntski deposit
(a) white kaolin and (b) red kaolin

Conclusions and Recommendations

1. X-ray diffraction analysis of white and red kaolin samples indicated that they contain more than 85% of aluminosilicate - kaolinite. The difference between the mineralogical composition of white and red kaolins is that the red kaolin contains 3.6% hematite (which results in its red colour).

2. It was experimentally determined that the pH_{PZC} of red kaolin is higher than the pH_{PZC} of white kaolin (8.2 > 6.5). This suggests that these two types of kaolin are capable of adsorption in acidic and slightly acidic aqueous media. Red kaolin is capable to adsorb pollution in alkaline waters.

3. It was established that the Ni^{2+} adsorption capacity of red and white kaolins depends on their mass. In a certain value range, with the increasing kaolin dose, the adsorption capacity decreases. This is mainly due to the saturation of kaolin surfaces and their electrostatic mutual repulsion in water (negatively charged kaolinite particles), which covers the site for Ni^{2+} adsorption.

4. The analysis of the calculated R2 coefficient showed that the adsorption of Ni^{2+} by red and white kaolins occurs according to the Langmuir model and the adsorption of Ni^{2+} is of a monolayer type.

5. Adsorption of Ni^{2+} by both kaolins is possible both in distilled water and in water characterized by total dissolved solids 2.5 g/L. The value of adsorption capacity depended on water total dissolved solids; the adsorption capacity of Ni^{2+} decreased with its increase, but it may be used to treat mining-impacted waters in reservoirs.

6. To ensure the ecological and economic effect of using the investigated kaolins, it was determined that the accumulation lakes of mine waters from the Kryvyi Rih iron ore basin (Kryvbas), Ukraine are most closely located to the kaolin quarries.

7. The synergy effect, including the simultaneous management of the material stored in heaps, and its direct application for reclamation of mine water reservoirs, enforces the use of the proposed concept interchangeably or predominantly concerning the use of organic sorbents and zeolites.

8. Regarding the chemical composition of mining waters in the vicinity of the studied kaolin quarry ($pH_{pzc} > 7.5$), a possible using of white kaolin or other potential natural sorbents, namely zeolite, is excluded. Using the most popular natural Ukrainian zeolite sorbent, the deposits of which are concentrated in the western part of Ukraine has a number of disadvantages. Crucial is the geographical location of the working quarry (over 1,200 km), the need for additional mechanical grinding, and most importantly its pH_{pzc} of approximately 6.5-6.8.

9. In order to develop the technological key, it seems necessary to conduct more extensive research on the sorbent properties of red kaolin in relation to other pollutants.

10. Transition is recommended to the 5th stage of Technology Readiness Level (TRL) which concerns the validation of the developed prototype in an environment similar to the real one, on larger samples under conditions of a system imitating the real system.

Referents

1. Rey, V.; Ríos, C.A.; Vargas, L.Y.; Valente, T.M. Use of Natural Zeolite-Rich Tuff and Siliceous Sand for Mine Water Treatment from Abandoned Gold Mine Tailings. *J. Geochem. Explor.* **2021**, *220*, 106660, doi:10.1016/j.gexplo.2020.106660.

2. Haddaway, N.R.; Cooke, S.J.; Lesser, P.; Macura, B.; Nilsson, A.E.; Taylor, J.J.; Raito, K. Evidence of the Impacts of Metal Mining and the Effectiveness of Mining Mitigation Measures on Social–Ecological Systems in Arctic and Boreal Regions: A Systematic Map Protocol. *Environ. Evid.* **2019**, *8*, 9, doi:10.1186/s13750-019-0152-8.

3. Worlanyo, A.S.; Jiangfeng, L. Evaluating the Environmental and Economic Impact of Mining for Post-Mined Land Restoration and Land-Use: A Review. *J. Environ. Manage.* **2021**, *279*, 111623, doi:10.1016/j.jenvman.2020.111623.

4. Milićević, S.; Vlahović, M.; Kragović, M.; Martinović, S.; Milošević, V.; Jovanović, I.; Stojmenović, M. Removal of Copper from Mining Wastewater Using Natural Raw Material—Comparative Study between the Synthetic and Natural Wastewater Samples. *Minerals* **2020**, *10*, doi:10.3390/min10090753.

5. Shirin, S.; Jamal, A.; Emmanouil, C.; Yadav, A.K. Assessment of Characteristics of Acid Mine Drainage Treated with Fly Ash. *Appl. Sci.* **2021**, *11*, doi:10.3390/app11093910.

6. Trach, Y.; Tytkowska-Owerko, M.; Reczek, L.; Michel, M. Comparison the Adsorption Capacity of Ukrainian Tuff and Basalt with Zeolite–Manganese Removal from Water Solution. *J. Ecol. Eng.* **2021**, *22*, 161–168, doi:10.12911/22998993/132605.

7. Bhattacharyya, K.G.; Gupta, S.S. Adsorptive Accumulation of Cd(II), Co(II), Cu(II), Pb(II) and Ni(II) Ions from Water onto Kaolinite: Influence of Acid Activation. *Adsorpt. Sci. Technol.* **2009**, *27*, 47–68, doi:10.1260/026361709788921614.

8. Bhattacharyya, K.G.; Gupta, S.S. Kaolinite, Montmorillonite, and Their Modified Derivatives as Adsorbents for Removal of Cu (II) from Aqueous Solution. *Sep. Purif. Technol.* **2006**, *50*, 388–397.

9. Gupta, S.S.; Bhattacharyya, K.G. Adsorption of Ni (II) on Clays. *J. Colloid Interface Sci.* **2006**, *295*, 21–32.