Heavy metals removal from wastewater by applying natural clay as adsorbent

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Abstract:
The study of natural available clay adsorbent for heavy metal removal was performed. Copper, nickel, and chromium solutions were prepared. The particle size and the zeta potential of clay sample were determined. The adsorption efficiency was studied in model solutions of enumerated heavy metal ions solution. The concentration of ions was determined spectrophotometrically. The influence of clay mass, contact time and ions interaction on adsorption efficiency were studied. The contact time was set to 30, 60, 120, 180 and 1440 minutes. Adsorption was the highest at the highest clay mass. The best adsorption efficiency was achieved with copper ions at 99.4 %. For nickel ions 58 % and for chromium ions 45 %. If three component system was studied the efficiencies were slightly lower, determined at 81.2 % for copper, 47 % for nickel and 29.4 % for chromium ions.

Key words: adsorption, clay, copper, nickel, chromium, spectrophotometry

1. Introduction

Water is a good solvent that dissolves both various beneficial as well as hazardous compounds. Its quality is decreasing due to worldwide pollution, especially industrial pollution associated with the use of many different heavy metals. Consequently, water is polluted by these metals. These metals are very long-lived and accumulate in the bodies of humans and animals. For instance, high levels of copper in the human body can damage the central nervous system and mucous membranes. In addition, nickel slows down the function and operation of enzymes and hormones. Excessive chromium content causes stomach and intestinal irritation and high temperatures [1].
Adsorbents such as activated carbon of various natural origins, zeolite, and clay are being studied and developed for the removal of heavy metals from aqueous systems and wastewater as well as from soil. Clay is a very efficient adsorbent for the removal of heavy metals from water solutions due to the content of exchangeable ions such as Na^+, Ca^{2+} and K^+. [2] Most clay minerals are negatively charged and are used for the removal of metals from wastewater. They also have a large surface area.

2. Heavy metals in wastewater

Heavy metals are a group of metals with the high density and are harmful to humans even at low concentrations. Among the heavy metals most dangerous are mercury, lead, cadmium, and also copper, arsenic, nickel, zinc, chromium. They differ from organic compounds which are readily biodegradable, while mentioned heavy metals are non-biodegradable and accumulate in human body. Heavy metals could be found in Earth crust, thus they are natural materials, however, they are accumulating due to human pollution. The Decree on the emission of substances and heat discharge of wastewater into water and public sewerage determines the limits of selected heavy metals. [3] In Table 1 some selected heavy metals and concentration's limits are presented

Table 1 Limit values for selected heavy metals [3]

Heavy metal	Limit value (mg/l)	Annual limit value (g/year)
Cu	0.5	500
Ni	0.5	500
Cr	0.1	100
Hg	0.005	20
Al	3.0	3 000
Mn	1.0	1 000

Copper forms complex substances with organic matter and is adsorbed into claystone and iron, alumina, and manganese oxides. It is among less mobile microelements and is of natural source. The soil is polluted by copper due to fertilizers, bactericides, fungicides, which are used in agriculture, but also copper origins from mining and different types of industry [4].
Nickel is generally found in low concentrations in nature, the percentage is around 0.01 %. The application in steel and other metal products processing causes pollution. Nickel could be found in air, water, and food in increased concentration. Cancer of lungs and oesophagus are caused by nickel poisoning. Also, chronical bronchitis, dermatitis and heart damages are not rare. [4].
Chromium is found in rocks, animals, plants, and soil. Chromium compounds are bound in soil in the form of precipitates, which are persistent and can enter water sources. [4] Chromium is used in metal alloys, protective

coatings for metals, magnetic types, cement, and paints. Chromium (VI) compounds are known to be carcinogenic to humans, while chromium (III) compounds are an essential nutrient in small doses. It causes allergic reactions when it comes into contact with the skin. High concentrations cause damage to the liver, lungs and nervous system.

3. Clay as natural absorbent

Clay has formed as transformation of volcanic and metamorphous rocks into clay minerals, such as kaolinite and chlorite [5]. The composition of minerals differs among each other; however, the main component are hydrated aluminium silicates with sodium, potassium and calcium oxides. Properties which are characteristic for all clay minerals are connected to chemical and multilayer structure. Clay minerals have high affinity for bounding water and ion exchange. The surface is charged and due to attraction also organic molecules could be bound to clay mineral. [5].

4. Experiments

The aim of the study was to determine the effect of clay mass on removal efficiency of different heavy metals from model solutions and from real samples of wastewater.

Clay

The clay was applied in form which is seen in Fig. 1, originating from Celje, Slovenia surroundings. The clay was analysed with emphasise on those elements which have the most effect on adsorption efficiency. Zeta potential was determined in order to assess the charge. The zeta potential measurements were based on mobility of particles in electric field. The value of potential above 30 V means stable colloid, and below unstable. Agglomerates are formed due to Van der Waals forces. Malvern Zetasizer nano sizer series was applied for the zeta potential and particle size determination. The measurements were made at 25°C. The average particle size of clay mineral was determined based on dynamic light scattering.

Figure 1: A sample of clay

Porosity and chemical composition were determined with electron microscope. Before analyses the Au layer was applied onto surface to achieve suitable electrical conductivity and stability of the sample. X-Ray Diffraction technique XRD was applied for determination of chemical composition.

4.1 Adsorption efficiency

Adsorption of heavy metals was studied at constant temperature at atmospheric pressure. The aim was to determine the efficiency of clay mass on individual metal ion removal as well as multiple metal removal efficiency in model solutions. In next step the removal of metals from real wastewater was studied. Solutions with following concentrations were prepared and served as working standard solutions: $\gamma(Cu^{2+})=\gamma(Ni^{2+})=50$ mg/l in $\gamma(Cr^{6+})=20$ mg/l.

The adsorption efficiency of heavy metals in dependence of clay mass was followed in model solutions of individual metal ion. The mass of 0.5 g, 1 g, 5 g, 7 g in 10 g of clay was weighted and diluted in 50 ml flask with deionised water. The solution was shake for 24 h.

In next step the adsorption efficiency of heavy metals in dependence of time was determined. The initial concentration of ions and concentration of remaining heavy metal ions in solution were measured after 30, 60, 120, 180, and 1440 min.

In next step the adsorption efficiency of heavy metals in dependence of mutual effect of ions at constant clay mass was measured. The initial concentration in model solutions were: $\gamma(Cu^{2+}) = \gamma(Ni^{2+}) = 25$mg/l and $\gamma(Cr^{6+}) = 20$ mg/l. The adsorption of following ions mixture on clay was studied: copper-nickel, copper-chromium, and

chromium nickel. Enumerated ion mixtures were prepared in 25 mL flask with model solution and 10 g of clay was added to each mixture.
Last part of experiments included the study of adsorption in wastewater samples at constant mass of clay 1 g. Sample A was taken during wastewater treatment in wastewater treatment plant and sample B represents the effluent from the treatment plant. The initial concentration of ions and concentration of remaining heavy metal ions in wastewater solutions were measured after 30, 60, 120, 180, and 1440 min.

5. Results

5.1 Clay characteristics

Figure 2 represents the average zeta potential in sample of clay at 25 °C. The value was -22,2mV. Negative value shows the high probability of attraction of positive ions. Since studied cations have positive charge, the high adsorption efficiency was expected. Also, literature review shows that cation adsorption could be high. [6].

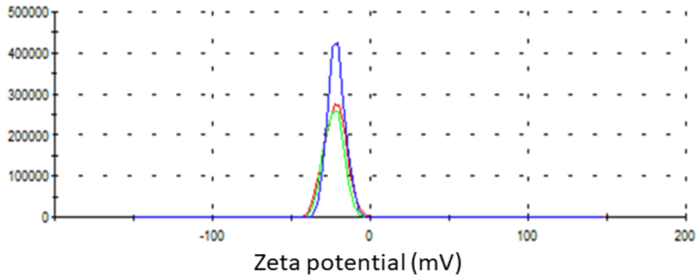

Figure 2 The average zeta potential

Fig. 3 shows particle size distribution after 3 measurements. The average value was 1285 nm for clay samples.

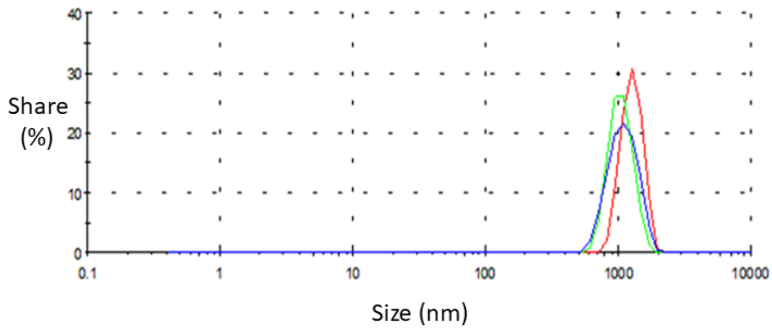

Figure 3: Average particle size

Table 2 shows the mas and atomic share of elements determined with XRD.

Table 2 The mas and atomic share of elements in clay

Element	Mass share (%)	Atomic share (%)
O	52.77	67.71
Mg	1.15	0.97
Al	13.87	10.55
Si	23.49	17.17
K	2.5	1.31
Fe	6.22	2.29
The Sum	100	100

The clay is very porous material with voids between the layers which is seen from SEM image in Figure 5.

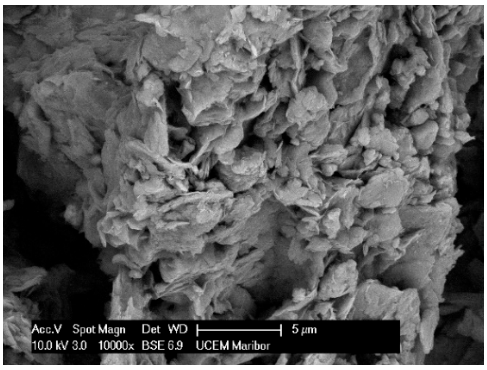

Figure 5: 10 000-time magnification of clay

5.2 Results of adsorption efficiency

Regarding the adsorption efficiency of heavy metal removal with different masses of clay, the literature overview showed high probability of metals removal. [6] The results showed that the removal efficiency improved by higher mass of clay mineral in accordance with literature and our expectations. The better adsorption is probably due to increased reactive adsorption sites in clay and higher probability of contact of adsorbent and ions [6]. Further, also contact time influences the adsorption capacity. The adsorption rate is the highest in the initial minutes of contact time and then it decreases until stationary phase is reached. At this moment all sites are fulfilled. In case of nickel adsorption onto clay, the increase of ions gradually increases with the nickel concentration [6]. If the clay mass also increases adsorption efficiency increased as seen from Figure 6. Similar adsorption flow is seen form Figure 6 for Cr, while copper removal efficiency was higher.

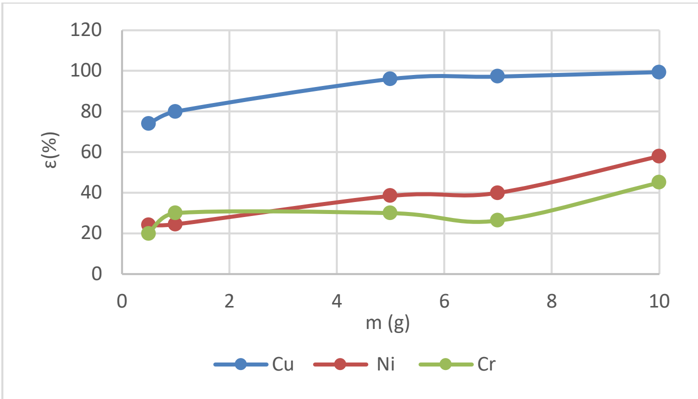

Figure 6: Efficiency of adsorbed ions in dependence of adsorbent mass

The comparison of adsorption after 24 hours between one and three component system was made. Figure 7 shows that adsorption in one component system was more efficient as it was also expected and the influence of ions as well as competition of all ions for free sites influences the efficiency.

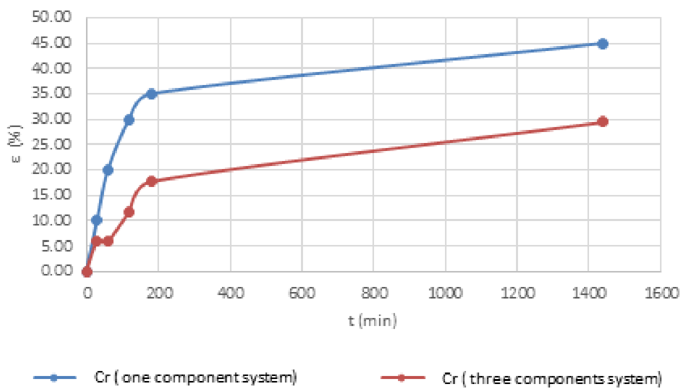

Figure 7: The comparison of adsorption after 24 hours between one and three component system for chromium

Table 3 shows initial concentrations of ions in pH dependence in different samples. The efficiency of samples of real wastewater A and B is shown in Table 4. The removal of ions from real wastewater samples A and B was comparable with the three-component system of copper, nickel, and chromium ions. The adsorption of chromium in sample A was 87.5 %, followed by copper at 85 % and nickel at 30 %. With sample B due to low copper content the concentrations were impossible to determine. Nickel adsorbed at 30 % and chromium at 60 % efficiency.

Table 3: Initial concentrations of individuals ions in samples of wastewater

	γ_0 (Cu^{2+}) (mg/L)	γ_0 (Ni^{2+}) (mg/L)	γ_0 (Cr^{6+}) (mg/L)	pH
Sample A	10	500	4	4,2
Sample B	/	0.5	0,05	8,3

Table 4: The adsorption efficiency in real samples A and B

	Sample A - ε (%) in pH				Sample B - ε (%) in pH			
t (min)	Cu^{2+}	Ni^{2+}	Cr^{6+}	pH	Cu^{2+}	Ni^{2+}	Cr^{6+}	pH
0	0	0	0	4.2	/	0	0	8.3
30	50	10	80		/	16	20	
60	70	22	80	4.1	/	20	40	8.1
120	78	24	82.5		/	24	60	
180	82	24	85		/	26	/	
1440	85	32	87.5	4	/	30	/	7.9

6. Conclusion

The main objective was to study the adsorption of heavy metals on clay. Firstly, characterisation was made. The zeta potential and particle size distribution showed -22,2 mV and 1285 nm. Chemical composition showed the main share of oxygen, silicious and aluminium. The SEM showed the porous material properties.
The efficiency of adsorption increased with the clay adsorbent mass. The highest efficiency was reached with copper ions: on 10 g of clay 99.4 % of ions were adsorbed with the initial value of 50 mg/L. Also, high adsorption efficiency was gained with nickel at 58 % and finally chromium ions at 45 %. The highest capacities were determined with 0.5 g adsorbent with copper at 3.7 mg/g, with nickel at 1.2 mg/g and chromium at 0.4 mg/g.
The adsorption of metals in one component system was more efficient in comparison with three component system as it was also expected. In three component system 20 % less ions were adsorbed as in one component system, while the competition of ions for free cites in major mechanism.
The removal of ions from real wastewater samples A and B was comparable with the three-component system of copper, nickel, and chromium ions. The adsorption of chromium in sample A was 87.5 %, followed by copper at 85 % and nickel at 30 %. With sample B due to low copper content the concentrations were impossible to determine. Nickel adsorbed at 30 % and chromium at 60 % efficiency.
Further investigations are going to focus on the influence of temperature, pH, and pressure on adsorption of heavy metal ions.

5. References

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