Original Research Article

The potential of bentonite as a low-cost adsorbent for the removal of heavy metal ions from multicomponent aqueous systems of the galvanic industry

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ABSTRACT

Waste water in the galvanic process contains high concentrations of heavy metals that pose a direct danger to humans and the environment. Conventional methods for their removal are quite expensive and generate a large amount of waste. The development of new and improvement of existing methods for the removal of heavy metals from galvanic wastewater are the subject of many studies.

Adsorption is one of the methods that is intensively researched, and biosorption as a subtype of adsorption includes the application of natural materials. The aim of the work is to investigate the possibility of using natural bentonite for the removal of heavy metal ions from multi-component water systems of the galvanic industry.

For this purpose, the physico-chemical characterization of natural bentonite was performed, and then the influence of pH value, time and temperature on the adsorption efficiency was examined.

The results of adsorption showed that natural bentonite can be used as an adsorbent for the removal of heavy metal ions from waste galvanic waters, and that at pH 5 it achieves the maximum removal efficiency for Cu(II):Cr(III):Ni(II) ions in the percentage ratio 100 : 99.990 : 99.998.

Keywords: bentonite, heavy metals, adsorption, wastewater, galvanic industry.

1. INTRODUCTION

One of the serious consequences of accelerated industrial development is environmental pollution with heavy metals. Heavy metals are very persistent and non-biodegradable, and depending on the type and concentration of the metal, they can also be toxic . The increase in the concentration of metals in the environment is most often a consequence of various human activities related to the industrial use of those metals. One of them is electroplating, a procedure in which heavy metals are used to coat organic and inorganic materials in order to protect against corrosion . Galvanic waste water represents a great danger for watercourses, whether it is in the way that it flows indirectly through the public drainage system, if it is not purified before discharge to the level prescribed by legal legislation, or in the way that it flows directly into them. For this reason, the treatment of galvanic wastewater is extremely important for the preservation of balance and biological diversity . Various methods can be used to remove heavy metals from waste water, such as coagulation, flocculation, membrane filtration, ultrafiltration, chemical treatment, electrodialysis, photocatalysis, reverse osmosis, ozonization and others. Among them, adsorption stands out as more desirable due to its characteristics such as high efficiency, simplicity, low cost, as well as the possibility of using various natural adsorbents . In addition, this process can remove or reduce various types of pollutants and thus has a wider application in the purification of polluted waters . In recent years, zeolites, clays, activated carbon, orange peel, etc. have been used as potential adsorbents for the removal of heavy metal ions and above all, the application of galvanic wastewater removal can be found as a small research result . Large specific surface area, high ion exchange capacity, chemical and mechanical stability are properties of clay, which have an affinity for the adsorption of cationic, anionic and neutral metal forms . Thanks to its good properties, low price and wide distribution, bentonite has become a material that is increasingly used in environmental protection. Bentonite is clay of volcanic origin, which contains the clay mineral montmorionite as its main component. It belongs to the group of clay minerals 2:1, a subgroup of dioctahedral smectites, whose basic structural unit consists of two tetrahedrally coordinated layers of silicon ions, between which one octahedral layer is built of aluminum ions. As a result of isomorphic substitution, which implies the replacement of Si^{4+} in the tetrahedral layers with Al^{3+} and the possible incorporation of Fe^{2+} or Mg^{2+} in place of Al^{3+} in the octahedral layer, a permanent negative charge appears on the montmorionite particles. Therefore, the aim of this work is to examine whether bentonite can be used to remove Cu(II), Cr(III) and Ni(II) ions from the galvanic industry wastewater.

2. material and methods

The material examined in this work is natural bentonite originating from Šipovo, Bosnia and Herzegovina. The following methods shown in Table 1. were used for the physical and chemical characterization of the material as well as for monitoring the adsorption processes.

Table 1. Methods used for physical -chemical characterization of bentonite

Parameters		Methods
Moisture and ash content (%)		Gravimetric Method
Total capacity of echangeable cations (mmol g^{-1})		Standard ion exchange method with NH_4Cl
Adjusting and measuring the pH value		Potentiometric method using a pH-meter with a combined electrode brand Mettler Toledo 220.
Chemical composition (%)		X-ray diffraction analysis (XRD) and X-ray fluorescence analysis (XRF) using a Bruker D4 ENDEAVOR, Germany device with a 2.4 kW power generator.
Surface area (m^2g^{-1})		Nitrogen adsorption method at 77K using Micromeritics Tristar II Plus Analyzer.

		Calculation of the specific surface area of the sample by the integrated software was carried out using the standard Brunauer-Emet-Teller (BET) equation.

Biosorption experiments were conducted using prepared synthetic solutions of $CuSO_4$ x $5H_2O$, $CrCl_3x6H_2O$, $Ni(NO_3)_2x6H_2O$ with distilled water, concentration 1000 mg/L. The pH value was adjusted with 0.1 M/0.01 M NaOH and HNO_3. The experiments were performed in batch conditions at a rotation speed of 300 rpm. To determine the concentration of Cu(II), Cr(III) and Ni(II) ions in synthetic aqueous solutions before and after sorption, atomic absorption spectrophotometry was used, using an Aanaylst 200 spectrophotometer. Adsorption capacity (qt) as well as process efficiency E (%) were calculated using the following relations:

(1)

(2)

where is :

q_t- adsorption capacity that shows the amount of adsorbed matter per unit mass of adsorbent in time t (mg g^{-1});

c_i - initial metal concentration in the solution (mg L^{-1});

c_t – metal concentration in the solution at time t (mg L^{-1});

v- volume of solution (L);

m-mass of adsorbent (g).

3. results and discussion

3.1 Physical and chemical characterization of bentonite

The analysis of moisture and ash content showed that the bentonite sample contained 10.097% moisture and 81.98% ash. Depending on the applied temperature regime, heating the clay leads to dehydration to a certain degree. The loss of adsorbed water at temperatures from 100 to 200 °C affects the macro, meso and microporosity of the clay, as well as its plasticity. The moisture content can be considered relatively low, that is, the adsorbent does not retain a large amount of water in its structure, which is why it can be stored in the air, without particle sticking and granulation changes. This feature is of particular importance for easy handling of the adsorbent when used in larger water purification systems.

Figure 1. shows the results for the point of zero charge (pH_{pzc}), which is an important factor in determining the nature of active sites on the surface of the adsorbent .The point of zero charge for bentonite was pH= 9, which means that the surface below this pH value will be positive

charged and electrostatically attract anions, while above this pH value it will be negatively charged and attract cations .

Fig.1. Point of zero charge of bentonite

The cation exchange capacity (KIK) of bentonite represents the ability of the adsorbent to adsorb cations from aqueous solutions. One of the mechanisms that can participate in the process of removing metal ions is ion exchange. Table 2. shows the ion exchange capacity of bentonite. The total exchange of all cations was 0.6147 mmol g^{-1} and represents a slightly lower value compared to KIK smectite (0.80-1.50 mmol g^{-1}), which is a consequence of the presence of non-clay materials, in addition to montmorionite .

Table 2. Content of exchangeable cations in bentonite

Exchangeable cations		Value (mmol g^{-1})
Ca^{2+}		0.180
Mg^{2+}		0.043
K^{+}		0.011
Na^{2+}		0.380

Based on the obtained results, it can be seen that the Na ion is dominant compared to other metals, which means that the Na ions from bentonite will probably be exchanged with Cu (II), Cr (III) or Ni (II) ions, according to the principle of ion exchange, and that ion exchange plays a major role in to the process of binding the examined ions, while the other easily exchangeable ions are exchanged in the following order: Ca < Mg < K.

The obtained results of the chemical composition of bentonite shown in Table 3. showed the presence of SiO_2 (51.67%) and Al_2O_3 (30.21%), which indicates that it is an aluminosilicate material. Oxides such as Fe_2O_3, Na_2O, CaO, MgO, K_2O are present in smaller amounts. A high proportion of Al_2O_3 indicates the presence of aluminum oxides or the substitution of aluminum with silicon, while the presence of MgO, CaO and N_2O indicate that these are the main exchangeable cations in bentonite .

Table 3. Chemical composition of bentonite determination by XRF analysis

Compounds		Value (%)
SiO_2		51.67
Al_2O_3		30.21
Fe_2O_3		7.49
Na_2O		3.29
CaO		3.26
MgO		2.60

K_2O		0.37

Figure 2. shows the diffractogram obtained by X-ray diffraction analysis, where the intensities are recorded as a function of the angle 2θ. By numbering each diffraction maximum (from the smallest to the largest angle 2θ) and determining its intensity and corresponding angle 2θ, all the necessary parameters were determined that enable the calculation of the d value (interlayer distance), which is characteristic for each material. The analysis of the diffraction maxima confirmed the presence of montmorionite (M), while the other crystalline phases were quartz (Q) and cristobalite (C) . Similar values of the diffraction maximums on the bentonite sample were also obtained by Petrović R. et al. and Ranđelović M. et al. .

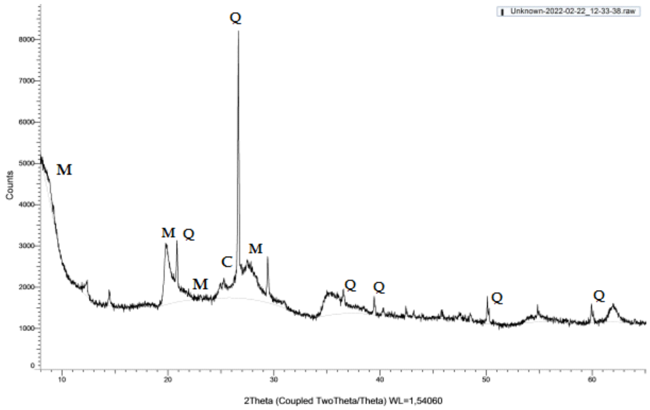

Fig.2. XRD analysis of bentonite

The calculation of the specific surface area of the sample was done using the adsorption method at 77K and using the standard Brunauer-Emet-Teller (BET) equation, which is the most commonly used model for determining the specific surface area of porous materials. The specific surface area of bentonite determined by the BET method was 80.9976 m^2g^{-1}, pore volume 0.064904 cm^3g^{-1} and average pore volume 32.052 Å. (Table 4.) The analysis confirmed that the used bentonite has a large specific surface which is desirable for efficient adsorption. Similar values were obtained by other authors who used natural bentonite to remove metal ions: 69.34 m^2g^{-1}; 88.80 m^2g^{-1}; 86.63 $m^2g\text{-}^1$.

Table 4. Value of the specific area surface

Characteristics		**Value**
BET surface area Pore volume (p/p°=0.95) Average pore width Average pore diameter		80.9976 m^2g^{-1} 0.0649 $cm^3\ g^{-1}$ 65.922 Å 32.052 Å

3.2. The influence of process parameters on the adsorption process

3.2.1 The influence of the initial pH value of the solution

The influence of the initial pH value of the solution on the removal of metal ions by bentonite was investigated in solutions in which the initial concentration of Cu(II), Cr(III) and Ni(II) ions was 1000 mg/L. Initial pH values were set to: 2.0; 3.0; 4.0; 5.0; and 6.0 using 0.1 mol/L HNO_3 or NaOH solution. The solid/liquid phase ratio was 1 g/50 mL. The suspensions were mixed at 300 rpm, and the analysis results obtained are shown in Figure 3. From the obtained results, it can be seen that the adsorption capacity as well as the efficiency of heavy metal removal increases with increasing pH values for all metal ions, with the maximum adsorption capacity ~~capacity~~ achieved at pH 5 for Cu(II) ions 4.9999 mg/g; for Cr(III) ions 4.9999 mg/g; for Ni (II) ions 4.9998 mg/g. Minimal adsorption at high acidity of the solution could be explained by the high concentration and high mobility of H^+ ions, so hydrogen ions are preferentially adsorbed on sorption sites compared to metal ions Cu(II), Cr(III) and Ni(II), which indicates that the process, among other things, is characterized by ion exchange. As the pH value increases, the concentration of H^+ ions decreases, and the active sites of the clay undergo a deprotonation reaction and attract positively charged ions by electrostatic forces, which explains the higher efficiency of removing heavy metal ions . With the increase in the pH value of the solution, the adsorption capacity for all types of investigated heavy metal ions increases and at a pH value of 5.0 it reaches its maximum when 100% of copper, 99.999% of chromium and 99.998% have been removed.

Fig.3. Influence of pH value on adsorption Cu (II), Cr(III) and Ni(II) ions

(Adsorbent dose=1 g; Volume=50 mL; Initial concentration=1000 mg/L; Rotation speed:300 rpm)

3.2.2 The influence of the contact time on adsorption process

The influence of the contact time of the adsorbent with heavy metal ions: Cu(II), Cr(III) and Ni(II) on the adsorption of heavy metal ions was examined at different contact times of 5, 10, 20, 40 and 60 min. Only contact time while other operating parameters were constant. The obtained results (Figure 4.) show that the highest efficiency is achieved during the first 10 minutes for Cu(II) ions 100%, that is, during 20 minutes for Cr(III) ions 99.999% and for Ni(II) ions 99.998%. This phenomenon is attributed to the fact that at the beginning of the adsorption process there are a large number of free binding sites on the surface of the adsorbent, which is why the process takes place very quickly. Then, over time, the concentration of free metal ions in the solution decreases, as does the number of available binding sites on the surface of the adsorbent, which slows down the adsorption process. For some heavy metal ions, the removal efficiency in the first 10 min is as high as 80% . The high efficiency in the removal of metal ions achieved by this adsorbent can be related to the high ion exchange capacity.

Fig.4. Influence of contact time on adsorption Cu(II), Cr(III) and Ni(II) ions

(Adsorbent dose=1 g; Volume=50 mL; Initial concentration=1000 mg/L; pH =5; Rotation speed:300 rpm)

3.2.3 The influence of temperature on the adsorption process

Temperature plays a significant role in the adsorption process because it affects the balance and speed of the adsorption process . An increase in temperature for the exothermic adsorption process would result in a decrease in the removal efficiency of metal ions, while the opposite is true for the endothermic adsorption process However, it is desirable that the adsorption process takes place at ambient temperature to avoid additional cooling or heating . In order to examine the influence of temperature on the binding kinetics of the ions of the investigated heavy metals, the tests were performed at temperatures of 298, 308 and 318K (Figure 5). As can be seen in Figure 5., the maximum efficiency of removing Cu(II) ions was achieved at all temperatures, while for Cr(III) ions 99.99% and Ni(II) ions 100%, the maximum efficiency was achieved at 308° K. Based on the results, it can be concluded that the adsorption process is endothermic. The obtained results are in accordance with the research of Saad A. Aljlil et al.. .

Fig. 5. Influence of temperature on adsorption Cu (II), Cr (III) and Ni (II) ions (Adsorbent dose=1 g; Volume=50 mL; Initial concentration=1000 mg/L; pH =5; Time=60 min; Rotation speed:300 rpm)

3.3 Adsorption isotherms

The most important information about the understanding of adsorption processes is provided by the adsorption equilibrium, which is described by adsorption isotherms. In order to determine the equilibrium concentrations and establish the ratio of Cu(II), Cr(III), Ni(II) ions adsorbed on bentonite, the Freundlich and Lengmuir adsorption isotherm was applied. The Freundlich adsorption isotherm describes adsorption on a heterogeneous surface between adsorbent and adsorbate and confirms multilayer adsorption The Freundlich adsorption isotherm is represented by a linear equation:

(3)

where: qe- equilibrium adsorption capacity (mg g^{-1}), C_e- equilibrium concentration of adsorbate in the solution (mg/L), K_F and n constants of the Freundlich adsorption isotherm.

Langmur's adsorption isotherm refers to adsorption on an energetically uniform surface without transmigration of adsorbate on the surface of the adsorbent and interaction between adsorbed molecules . The Langmuir adsorption isotherm is described by the following linearized equation:

(4)

where: qe is the equilibrium adsorption capacity (mg g^{-1}), Ce- the equilibrium concentration of the adsorbate in the solution (mg/L), K_L - the Langmuir constant (L mg^{-1}) related to the adsorption energy, q_m- the maximum adsorption capacity (mg g^{-1}).

An important parameter when checking the Langmuir adsorption isotherm is the separation factor (R_L).

(5)

Table 5. shows the obtained values of adsorption isotherms. The best agreement of the isotherm model with the experimental data was determined based on the correlation coefficient R^2. From the obtained results, it can be seen that the experimental data for the removal of Cu(II) ions agree well with the Langmuir and Freundlich isotherm model, because the value of the correlation coefficient R^2 in both cases is 1. On the other hand, the value of the correlation

coefficient R^2 for the adsorption of Cr(III) and Ni(II) ions according to the Langmuire isotherm model is higher than the values according to the Freundlich isotherm model where it is 0.8767 and 0.7808.

The Langmuir model provides an important parameter, q_m, which represents the theoretical maximum adsorption capacity, which corresponds to the complete coverage of the monolayer, and this value for Cu(II) and Cr(III) is higher than the experimental one, which shows that bentonite can adsorb higher concentrations of these metals. On the other hand, the experimentally obtained adsorption capacity is higher for Ni(II) ions than the theoretically calculated maximum adsorption capacity, which suggests that it is probably a combination of two successive adsorption processes, physisorption and chemisorption. The separation factor, R_L, determined by the Langmuir constant provides information on whether the adsorption reaction is favored, reversible, or irreversible. The displayed value is in the range $0 < R_L < 1$, which suggests a favorable adsorption for all tested metal ions on bentonite as adsorbent. On the other hand, the Freundlich adsorption isotherm describes adsorption on a heterogeneous surface, where the parameter K_F refers to the binding capacity of the adsorbate, and the value of the constant n indicates the affinity of the adsorbent for the adsorbate For all three adsorbents, this constant has a value slightly greater than 1, which according to Wan Nagh et al. indicates that adsorption is favored . Shaymaa Talib Hussain et al. gave a good agreement with the mentioned isotherm models for the adsorption of Cu (II) ions on bentonite; Zuzana Melichová et al. , S. Kubilay et al. and many other authors.

Table 5. Value of adsorption isotherm parameters

Isotherm models	**Cu (II)**	**Cr (III)**	**Ni(II)**	
Freundlich isotherm	5.033	7.528	4.994	
K_F	100000	50000	3333.33	
n	1	0.8767	0.7808	
R^2				
Lengmuir isotherm				
K_L	5	$3.50 \cdot 10^{-7}$	$9.99 \cdot 10^{-5}$	
Q_m	5	5	4.992	
R_L	$2 \cdot 10^{-4}$	0.996	0.909	
R^2	1	1	1	

4. CONCLUSION

The results of this research indicate that the tested bentonite sample used as an adsorbent consists predominantly of the clay mineral montmorionite, and that quartz and cristobalite are used as applications. Bentonite basically consists of SiO_2 (51.67 %) and Al_2O_3 (30.21%), which indicates that it is an aluminosilicate material with a large specific surface area (80.9976 m^2g^{-1}) and a high cation exchange capacity (0.6147 $mmolg^{-1}$).

The adsorption results showed that the adsorption capacity as well as the removal efficiency increase with increasing pH values for all metal ions, with the highest adsorption capacity achieved at pH 5, for Cu (II) 4.9999 mg/g; Cr (III) 4.9999 mg/g; for Ni (II) 4.9998 mg/g, and the efficiency of the Cu (II) adsorption process 100%; Cr (III) 99.999%, Ni (II) 99.998%. The maximum efficiency of Cu (II) removal was achieved at all temperatures, while for Cr (III) 99.99% and Ni (II) 100% maximum efficiency was achieved at 35°C, which indicates that the adsorption process is endothermic.

The experimental results of the adsorption of Cu (II) metal ions are in good agreement with the Langmuir and Freundlich theoretical models, while for Cr (III) and Ni (II) ions they are in better agreement with the Langmuir adsorption model.

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