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ELECTROPLATING WASTEWATER TREATMENT USING A ROMANIAN BENTONITE

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ABSTRACT. In this study we considered the possibility to remove iron and zinc ions from electroplating wastewaters using a clay mineral (bentonite). We worked with a bentonite cropped from Valea Chioarului, Maramures County, Romania, deposit. The bentonite sample was characterised by means of surface specific area (BET), chemical analysis, X-ray diffraction, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and Fourier transformed infrared (FTIR) spectroscopy. Electroplating wastewaters provided by SC BETAK SA Bistrita, with an initial iron and zinc content of 1100.7 g Fe_{total}/dm^3 and 126.8 g Zn^{2+}/dm^3 respectively, and a pH of 0.5, were used. The heavy metal ions removal process was realised in a batch reactor (static regime) using a micronised bentonite sample (d < 4.5 µm). This type of bentonite proved to be efficient in the iron and zinc ions removal (100% removal efficiency).

Keywords: Clay mineral, bentonite, montmorillonite, electroplating wastewaters, zinc ions, iron ions.

1. INTRODUCTION

Galvanic plating workshops consume a great amount of water in the technological process (plating, acid treatment) as well as in the plated pieces washing process. The most important wastewaters containing heavy metal ions resulted in the technological process are used electrolytes (concentrated solutions) and acid washing solutions (semi-concentrated solutions).[1,2] These waters will have a high content of heavy metal ions and low pH values.[1] In the last years, the problem of re-utilisation of these waters, after a proper treatment, became an important issue.[2] The classical technology applied in the majority of the industrial units, is dilution until the maximum allowable concentration is reached. Taking in account the increasing number of galvanic plating workshops, this classical technology reached its limits.

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Heavy metal ions can be removed from wastewaters using physical, chemical and electrochemical methods. A variety of methods such as precipitation, solvent extraction, vacuum evaporation, membrane technologies (microfiltration, ultrafiltration, reverse osmosis), adsorption and ionic exchange, electrolysis, or electrodialysis are available.[3-14]

Due to the high toxicity of the heavy metal ions (zinc, lead, cadmium, etc.) maximum allowable concentrations for discharging in surface water streams are very small.[15] In order to achieve the maximum allowable concentrations imposed for discharged waters according to specific legislation, combined methods are frequently used.

The usage of natural mineral raw materials (zeolitic volcanic tuffs, clays, porous silicatic rocks etc), even if feasible, is still approached only as research proposals, as a result of the incomplete knowledge on their amounts, quality and behavior, and especially on the possibilities of their regeneration after technological usage.

On a global scale, clays (clay minerals), besides the zeolites proved to be very suitable materials for various industrial activities (special building materials, ceramics, etc.).

Clay minerals are aluminium hydrosilicates, crystallized in monoclinic system, characterized by planar reticular structures. Stratified structure of mineral clays is determined by the combination in one reticular plan (structural unit) of two cationic layers, one layer in which silicon is coordinated tetrahedric with O·OH (tetrahedric level Te) and one layer in which aluminium is coordinated octahedric with O·OH (octahedric level Oc). These layers are bonded between them with van der Waals bonds forming the structural unit. According to the numbers of Te and Oc layers, clay minerals are classified in 1Te:1Oc (*eg*. kaolinite), 2Te:1Oc (*eg*. montmorillonite) and 2Te:2Oc (*eg*. chlorite). The layered structure of the clay minerals and presence of isomorphous replacement of Si^{4+} with Al^{3+} (negative charge compensated by Na^{+}, K^{+}, Ca^{2+} and/or Mg^{2+}) determines their main properties: hydration, swelling, water and organic compounds adsorption and ionic exchange capacity.[1,16] Clays have been found a large applicability also in depollution processes, purification of urban and industrial residual waters, protection of waste disposal areas or purification of industrial gases.[17-19]

Clay minerals of different types and with different modifications (organic modified, immobilised) were widely studied in the heavy metal ions removal processes from wastewaters. Between the clay minerals used to remove heavy metal ions from wastewaters, bentonite (Ca-, Na- or organic modified bentonite) and kaolin were mainly studied.[9-11,20-29]

Bentonite is a material composed of clay minerals, predominantly montmorillonite with minor amounts of other smectite group minerals, commonly used in drilling mud. Montmorillonite forms from weathering of volcanic ash, most often in the presence of water.

Montmorillonite is a phyllosilicate mineral, member of the smectite family, consisting of two tetrahedral layers and one octahedral layer (2Te:1Oc). The silicate tetrahedral layers have a slight negative charge (due to replacement of silicon atoms with Al, Mg and sometimes with Fe atoms) that is compensated by exchangeable ions in the intercrystallite region. The charge is so weak that the cations (in natural form, predominantly Ca^{2+}, Mg^{2+} or Na^{+} ions) can be adsorbed in this region with their hydrated shell. The extent of hydration produces intercrystalline swelling. Bentonite presents strong colloidal properties and its volume increases several times when coming into contact with water, creating a gelatinous and viscous fluid. The special properties of bentonite, with its main component smectite, hydration, swelling, water absorption, viscosity, tixotropy, make it a valuable material for a wide range of applications. Worldwide complex research work on clays evidenced a large range of usages based on the specific properties of clay minerals. The most important properties of bentonites are adsorption and ionic exchange capacity, properties which gives them exceptional qualities related to environmental protection technologies.[30-45]

In Romania, large bentonite deposits are known from the Transylvanian Depression or the extra-Carpathian area.

This paper presents the results obtained using a Valea Chioarului (Maramures County) bentonite sample, within the framework of an ample study regarding the uses of some clay minerals (different occurrences) from Romania, in wastewaters treatment. This bentonite sample was characterized and used to remove iron and zinc from wastewaters.

2. EXPERIMENTAL

2.1. Bentonite compositional and structural investigations

A representative sample of crude bentonite, (d < 4.5 μm), from Valea Chioarului (Maramures county) deposit was characterised by means of surface specific area (BET), X-ray diffraction, chemical analysis, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and Fourier transformed infrared (FTIR) spectroscopy.

2.2. Operating conditions

For the iron and zinc removal study we used electroplating wastewaters from SC BETAK SA Bistrita with an initial iron and zinc content of 1100.7 g Fe_{total}/dm^3 and 126.8 g Zn^{2+}/dm^3 respectively and a pH of 0.5. These waters were neutralised (from pH = 0.5 to 7.3), filtered and diluted hundred times. After these procedures the concentrations of the water sample (the initial concentration for the removal process) were 636.8 mg Fe_{total}/dm^3 and 833.3 mg Zn^{2+}/dm^3. Determination of zinc and iron ions in wastewaters was realised using a Jenway 6305 UV/VIS spectrophotometer after a prior centrifugation. Zinc determination was made at 420 nm (potassium ferrocyanide), while for iron we worked at 510 nm (ortho-phenantroline), according to Romanian standards.[46,47] The concentration and efficiency values calculated in this paper have to be looked as according to the precision limits of the determination methods. Experiments were carried out without any modification of temperature (room temperature).

The heavy metal ions removal process was realised in a batch reactor in static regime using 20 g of bentonite (d < 4.5μm) and 100 ml wastewater (bentonite : solution ration, 2:10).

The evolution of the wastewater treatment process was followed by means of variation of ions concentration in time, heavy metal ions removal efficiency (calculated from values of ions concentration at a moment *t* and initial concentration) and adsorption capacity (iron and zinc uptake).

3. RESULTS AND DISCUSSIONS

3.1. Petrographic results

The bentonite from Valea Chioarului (VCh) is usually greasy and has grey-greenish colour, and locally could be whitish or yellowish. The bentonite formed by hydrothermal alteration of an acid rock (rhyolite). Relicts of primary rhyolite structure are often present. From mineralogical point of view, the bentonite from Valea Chioarului ore contains montmorillonite (72-80%) and feldspar, micas, quartz and opaque minerals in lower quantities. The colloidal fraction contains 97-98.5% montmorillonite and 1.5-2.5% cristobalite.[17,48,49]

BET specific surface area was determined to be 57.6 m^2/g.

The X-ray diffraction diagram performed on random powder (Siemens Bruker, Cu Kα anticathode, 10° to 70° 2 θ, 2 degrees step) of the whole material indicated the massive presence of Na-montmorillonite, characterised by a (001) reflect at about 12.5 Å associated with a few percents of halloysite and/or kaolinite (in < 2 μ fraction), and cristobalite, quartz and feldspar in bulk sample (figure 1). Cristobalite generation was caused by the excess of silica resulted from the montmorillonitization process of the volcanic glass.

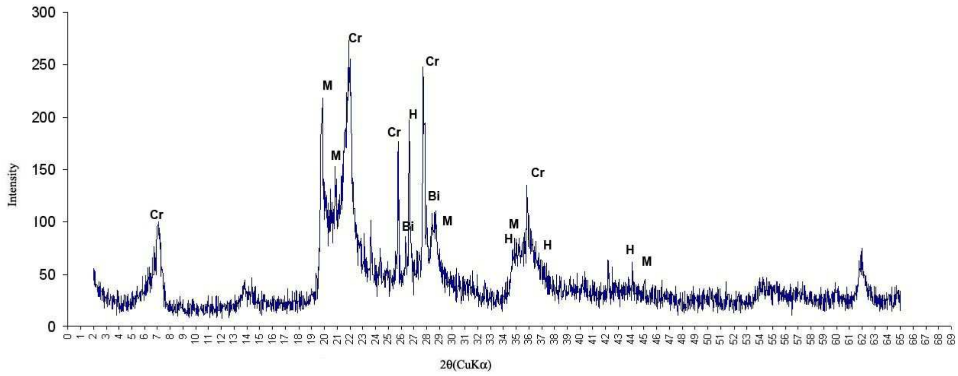

Figure 1. Powder X-ray diffractogram of a bentonite sample from Valea Chioarului (Maramures County); M=montmorillonit, Cr=cristobalit (silice), Bi=biotit, H=haloysit.

Surface morphology and local composition were established using SEM images, recorded with a scanning electron microscope JSM-5600 LV (JEOL), and EDS graphs, recorded with an Oxfrod Instruments EDS spectrometer. SEM images of the bentonite sample, figure 2, points out a gradual devitrification of the ground mass and the neoformation of smectite minerals. On the EDS spectra of the bentonite, figure 3, we could identify the elements forming the main structure of the clay mineral – Si, Al, Na and O – and also the accompanying elements – K, Ca, Mg, Fe, Ti, confirming the Na-montmorillonite type for our sample.

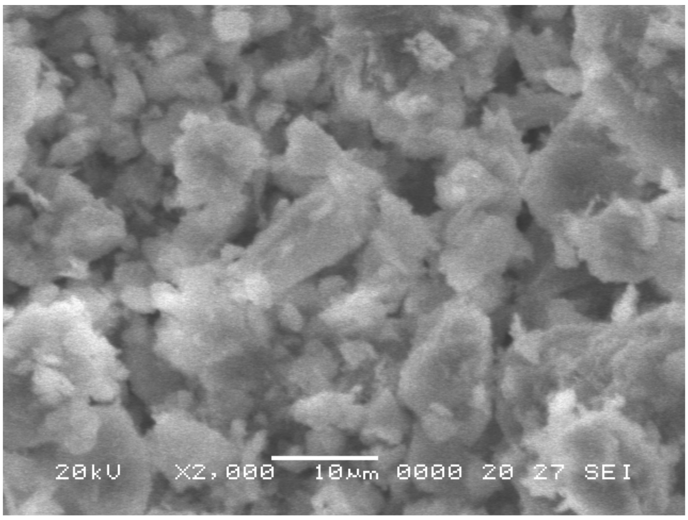

Figure 2. SEM image of a Valea Chioarului (Maramures County) bentonite sample.

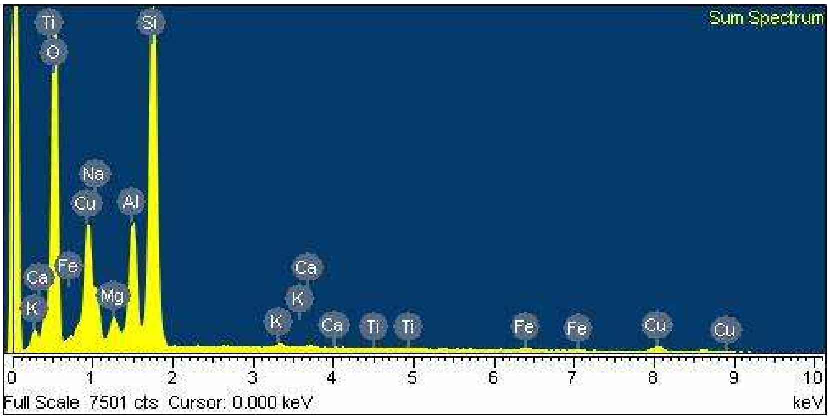

Figure 3. EDS spectra of a Valea Chioarului (Maramures County) bentonite sample.

The bulk chemical composition of the bentonite, table 1, indicates a very high content of silica, a low content of iron oxide and a higher content of Na as compared with other bentonite occurrences from Romania.

Table 1.
Chemical composition of the bentonite sample from Valea Chioarului (Maramures County).

Oxides, [%]	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	L.O.I.
VCh	70.71	0.31	13.90	1.48	3.35	0.60	2.20	0.55	6.90

Examination of the infrared spectra, recorded with a FTIR Jasco 6100, resolution 2 cm^{-1}, of the bentonite sample, figure 4, indicates the presence of specific bentonite peaks,[50-54] as follows: 3620.21 cm^{-1} – stretching vibrations of isolate hydroxyls and OH less firmly bond to the tetrahedrical outer layer, 3435.08 cm^{-1} – stretching vibrations of the structural OH and also the hydration water, 1632.45 cm^{-1} – angular deformation of hydroxyls from adsorbed water molecules (held in interlayers), 1089.58/1037.51 cm^{-1} – main bands corresponding to the stretching vibrations of Si,Al-O and 467.17/520.68 cm^{-1} angular deformations of Si-O-M bonds (M can be Al, Na, Fe).

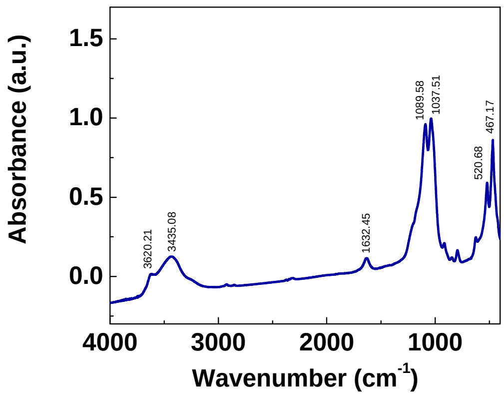

Figure 4. FTIR spectra of a Valea Chioarului (Maramures County) bentonite sample.

3.2. Heavy metal ions removal results

Evolutions of iron and zinc concentrations in static regime on the bentonite sample are presented in figure 5.

The heavy metal ions concentration drastically drops from the initial 636.80 mg Fe_{total}/dm^3 and 833.33 mg Zn^{2+}/dm^3, to 46.88 mg Fe_{total}/dm^3 and 2.68 mg Zn^{2+}/dm^3 respectively during the first 24 hours. After 48 hours zinc concentration drops to 0, while in case of iron the same thing happened after 72 hours. Therefore the values for removal efficiency are 100% in both cases. Evolution of the removal efficiencies values during the removal of heavy metal ions process is presented in figure 6. The efficiencies increase from 0 to 99.68% and 92.64% in 24 hours for zinc and iron respectively, reaching 100% after 48 hours for zinc and 98.17% for iron. After 72 hours the removal efficiency reached 100% for iron also.

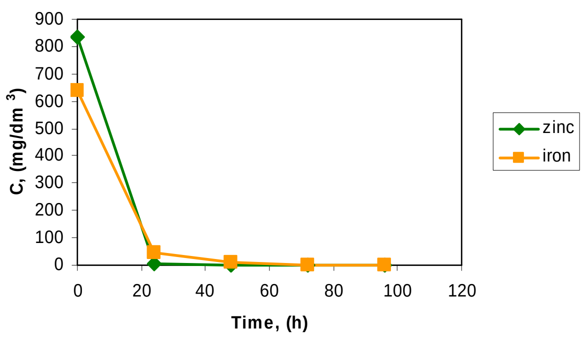

Figure 5. Concentration of zinc and iron ions as a function of time during the removal process.

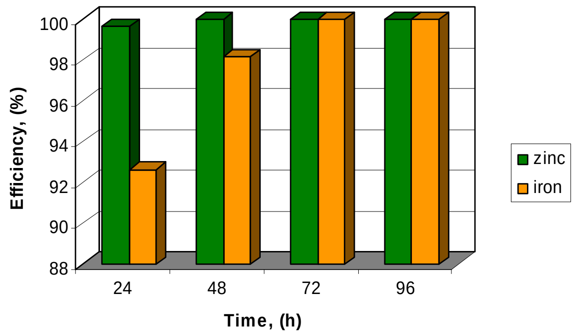

Figure 6. Variation of the removal efficiency during the zinc and iron ions adsorption process.

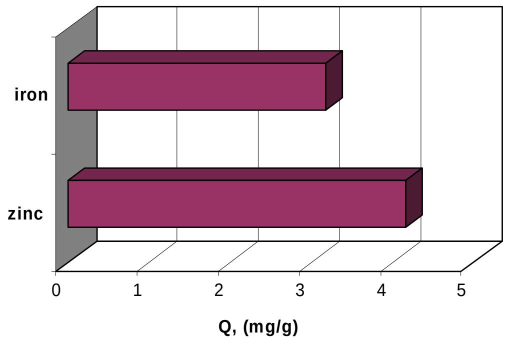

Figure 7. Maximum zinc and iron uptake on a bentonite sample from Valea Chioarului (Maramures County); static regime, 2:10.

If we compare the ionic uptake for iron and zinc, figure 7, it is easy to observe that zinc ions are adsorbed in a higher quantity, respecting the rule according to which, when two ions with similar charges exist in a solution, the one with the highest concentration will be adsorbed preferentially. The maxiumum values calculated for the ionic uptake are 4.17 mg Zn^{2+}/g solid and 3.18 mg Fe_{total}/g solid.

4. CONCLUSIONS

The heavy metal ions removal process took place with good results on the Valea Chioarului (Maramures county), Romanian bentonite sample, therefore the natural material (clay mineral) is considered to be an appropriate material to remove iron and zinc ions from electroplating wastewaters.

The ionic exchange experiments in static regime demonstrate that iron and zinc ions are hindered with high efficiencies. The ionic exchange efficiencies reached 100% value for both ions, faced to the initial concentration, in 48 and 72 hours for zinc and iron respectively.

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