EFFECT OF FRIENDLY SORBENTS ON BASE POLYMER NANOCOMPOSITES

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ABSTRACT

Clay-based superabsorbents were synthesized using sodium bentonite via radical copolymerization of acrylic acid and acrylamide at temperatures between 30°C and 45°C. Ammonium persulphate – tetramethylethylenediamine was used as an initiator oxidation-reduction system, and N,N'-methylene-bis-acrylamide as the cross-linked agent. The swelling behaviour of clay-based superabsorbent samples in aqueous solutions at different temperatures was investigated. The sorption processes of nickel ions from aqueous solutions were studied. It has been shown to influence the proportion of bentonite sorption kinetics of nickel ions from aqueous solutions of different concentrations. Clay-containing polymer composites can be used as friendly materials for wastewater treatment.

Keywords: bentonite, hydrogel, nanocomposite, waste treatment, nickel, absorption.

1 INTRODUCTION

Superabsorbent hydrogels are a type of rarely crosslinked hydrophilic polymers that can swell, absorb and retain huge volumes of water and other aqueous solutions. They are many fields of their applications, such as urban water waste treatment, ecology, agriculture, medicine, etc. [1]–[4].

One of the important questions of water treatment of industrial and urban regions is removal contaminants including heavy metal ions (Co^{+2}, Ni^{+2}, Cr^{+3}, etc.) from aqueous solutions into streams, lakes and rivers. The main sources of environmental pollution by nickel – enterprises of the mining industry, ferrous metallurgy, machine-building, metal-working, chemical, instrument-making and other uses in industrial processes various nickel compounds; thermal power plants running on heavy fuel oil and coal; vehicles. Significant amounts of nickel ions enter the waters with the wastewater industry.

Heavy metals are very toxic and dangerous compounds for human. A higher concentration of nickel, one of the heavy metals, in the living body usually leads to different allergic reactions (dermatitis, rhinitis, etc.), anemia, increased excitability of the central and autonomic nervous systems [5]. Nickel is one of the carcinogenic elements. The risk of cancer (lungs, kidneys, skin) is increased from chronic intoxication by nickel ions. It is known that the presence of nickel ions (Ni^{+2}), about 2 times more toxic than its complex compounds.

For cleaning waste water from the nickel ions physico-chemical methods are used, such as chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation and flocculation, flotation, electrochemical treatment, and etc. [1], [6]–[8].

Electrotreatments such as electrodialysis, membrane electrolysis and electrochemical precipitation have also contributed to environmental protection. It is known to extract 90% of Ni (II) from wastewater using electrochemical methods, but they are expensive because of high energy consumption [8].

The advantage of chemical precipitants is the simplicity. However, their use has several drawbacks: necessary to increase the pH of the wastewater to 11 to effectively remove ions

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Nickel and chemical deposition produces large amounts of sludge, which also requires further processing.

In general, coagulation–flocculation can treat inorganic effluent with a metal concentration in range from 100 mg/L to 1000 mg/L and also need pH adjustment to 11. At lower pH values colloidal substance with a negative charge may coagulate and the cationic Ni^{2+} ion cannot be removed very well [8].

Membrane filtration technology is a promising method of wastewater treatment by nickel ions due to its simplicity, high efficiency and space saving. To remove Ni(II) ions from contaminated wastewater in Taiwan and South Korea is used method of membrane filtration. It is shown that nanofiltration membrane (NTR-7250) on the base polyvinyl alcohol is used to remove nickel ions from real electroplating wastewater.

However, the high pressure (2.9 bar) and certain initial metal concentration are required for application to remove Ni(II) ions from wastewater.

Absorption is one of the most effective and economical methods of cleaning up waste water from heavy metal ions. To advantages of absorption can be referred flexibility in design and operation and the possibility of reversing use of absorbent by suitable desorption process.

Despite the existing variety of physical and chemical methods, they do not always meet the environmental safety and cost-effectiveness requirements. After wastewater treatment, the concentration of heavy metals remains relatively high. For example, when cleaning up waste water by electrodialysis in water remains 25% of heavy metals ions and when used dimethylglyoxime – on the level of 0.3 mg/L [6].

Even very low concentrations 10^{-3} of heavy metals in water may alter the quality of aquatic environment. This can cause physiological, chemical and biological deteriorations of aquatic subjects.

In recent years, the applications of clay are often used for modification of polymer superabsorbents for good sorption, especially heavy metal ions, and mechanical and other properties [9]–[12].

The present study considers the clay-based superabsorbent on the base bentonite and acrylic polymers for removal of nickel ions from wastewater.

2 MATERIALS AND METHODS

2.1 Materials

Acrylic acid, acrylamide monomers, as N,N'-methylene-bis-acrylamide, served as a crosslinker, purchased from Sigma-Aldrich Chemie, were used as received. Sodium hydroxide, ammonium persulfate, bentonite were obtained from Merck and were used without any further purification. Acrylic acid was distilled under reduced pressure before use.

2.2 Preparation of SA composite

Acrylic acid (AA) was neutralized with sodium hydroxide solution (degree of neutralization of acrylic acid was $\alpha = 0.8$). Then acrylamide (AAm) was added to the solution. Ratio and concentration of monomers AA:AAm = 30 ÷ 70 mas.%. Crosslinker methylene-bis-acrylamide (MBA) was added to the monomer solution (0.1 mas.%). The mixture was poured into a beaker, which was equipped with a magnetic stirrer and thermometer. Bentonite was added to stirring solutions and stirring was continued for 20 min until homogeny mixtures were obtained. Concentration of filler varied from 0 to 60 mas.%. To start polymerization, oxidation-reduction system: ammonium persulfate – N,N,N',N'-tetramethylethylenediamine

(1:2) was added to the mixture as initiator. The temperature of mixture was increase to 40°C. Clay-based acrylic nanocomposite was prepared via radical copolymerization polymerization in the water for 4 h.

2.3 Absorbency measurement

The swelling of the clay-based polymer nanocomposites was investigated at 22ºC in different aqueous solutions by measurement of their weight at regular time intervals. The swelling degree (Q) was calculated by the following equation:

$$Q=\frac{m\text{-}m_0\left(1-\gamma\right)}{m_0\left(1-\gamma\right)},$$

where Q – degree of swelling of polymer sample, g/g; m – the mass of the polymer sample, g; m_0 – mass of initial polymer sample, g; γ – moisture content of a gel sample.

The water content in the clay-based polymer composites was estimated by drying it at 120ºC for 6 h to remove the water to constant weight. The water content was calculated as follows:

$$\gamma=\frac{(m_0-m_c)}{m_0},$$

where m_0 and m_c – weights of superabsorbent composition before and after drying, respectively.

The constant of swelling A is connected with Q(t) values the following equation:

$$\ln[Q_\infty-Q(t)]=\ln Q_\infty-At\ .$$

The constant of swelling rate At is determined as an angle tangent of the curve $\ln[Q_\infty-Q(t)]$ – t (min).

Heavy metal ions were detected by using UVIS spectrophotometer (Unico 2804). The amount of nickel ions adsorbed by the clay-based acrylic superabsorbents was calculated according to the equation:

$$Z=\frac{C_{init}\text{-}C_{final}}{C_{init}},$$

where C_{init} and C_{final} are the initial and final metal ions concentration in the solution (mol/L), respectively.

2.4 Elemental analysis

X-ray fluorescence method was used to determine the composition of bentonite (spectrometer “ARL Optim’X”).

3 RESULTS AND DISCUSSION

Elemental composition of native bentonite of using in this research is shown in Fig. 1 and Table 1.

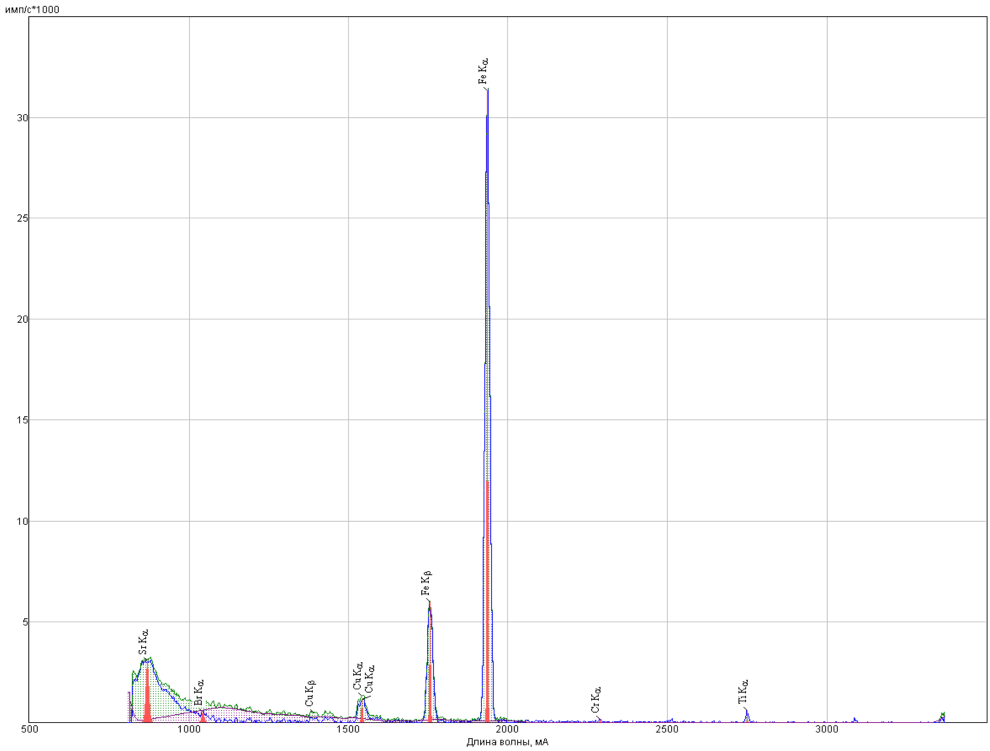

Figure 1: Spectrum of X-ray diffraction of bentonite.

Table 1: The elemental composition of the studied native clay – bentonite.

No.	Elements	Concentration, mass. %
1	Si	61.5
2	Al	12.0
3	Fe	11.5
4	Ca	2.1
5	Na	0.6
6	Other	12.3

A swelling process of clay-containing superabsorbents in solutions of heavy metal salts consists of two concurrent processes: diffusion of water molecules in the polymer network (swelling) and binding metal ions and ionic groups in polymer chain (collapse). The equilibrium degree of swelling of crosslinked copolymers in aqueous solutions of heavy metal ions is dependent on the nature of carboxyl groups and the concentration of the outer electrolyte solution. The stability polymer chain with polyvalent metal ions is determined by the structure of the polymer chain, the temperature of the solution, pH and concentration of metal ions, etc. Sorption characteristics of clay-based polymer materials were investigated in aqueous solutions of nickel chloride in the range $10^{-5} – 10^{-1}$ mole /L.

The increase of heavy metal ions concentration in the aqueous solution leads to decrease in the degree of swelling of the studied system.

Fig. 2 shows degree of swelling values of clay-based polymer compositions in nickel chloride solution at 22°C. As seen from Fig. 2, the increase of electrolyte concentration in the aqueous solution surrounding the bentonite-containing superabsorbents lead to decrease in the degree of swelling of the studied compositions, which also explains the effect of suppressing the polyelectrolyte.

The equilibrium degree of swelling of clay-based polymer superabsorbents with a different concentration of bentonite in $NiCl_2$ solutions were investigated (Table 2). It was shown, that a collapse of the acrylic nanocomposites is observed when the initial concentration of the surrounding $NiCl_2$ solution is 10^{-2} M.

Table 3 shows the kinetic parameters of swelling of clay-based polymer compositions in aqueous solutions of chloride nickel concentration at 22°C. As seen from Table 3, the increase of salt concentration leads to a raise in the rate of swelling and constants of swelling up to 1.5–2 times compared with the values of distilled water.

The results of the effect of salt solutions on the sorption of the clay-based polymer nanocompositions are given in Fig. 3. It was demonstrated that increasing the concentration of filler – bentonite particles leads to the raise of sorption concentration of the heavy metal ions at NiCl2 concentration of 10^{-3}M.

The dependence can be described in form of exponential equation: $D = 0.122e^{-0,31C}$, where D – sorption part of Ni-ions, C – concentration of clay, wt.%.

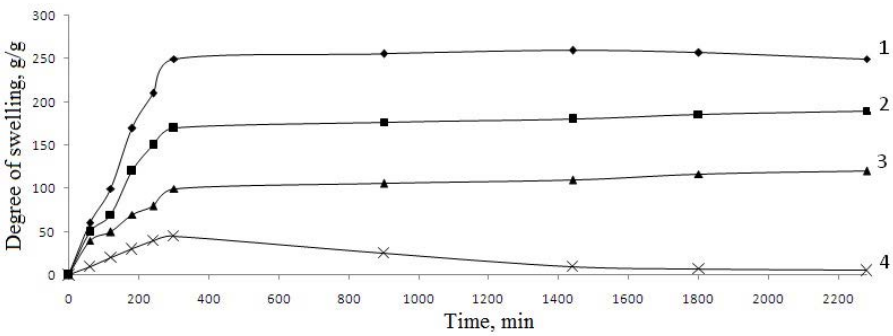

Figure 2: Swelling behaviour of clay-based polymer composition in $NiCl_2$ solutions at 22ºC. Bentonite concentration – 50 mas.%. Concentration of chloride nickel (M): 1 – 10^{-5}; 2 – 10^{-4}; 3 – 10^{-3}; 4 – 10^{-2}.

Table 2: Swelling behaviour of clay-based polymer composites in $NiCl_2$ solutions at 20°C.

Concentration of chloride nickel, M	The equilibrium degree of swelling of clay-based superabsorbents, g/g				
	Concentration of bentonite, 0 mas. %	Concentration of bentonite, 10 mas. %	Concentration of bentonite, 30 mas. %	Concentration of bentonite, 50 mas. %	Concentration of bentonite, 60 mas. %
10^{-5}	350	320	280	250	190
10^{-4}	210	190	170	180	110
10^{-3}	125	150	140	110	70
10^{-2}	25	45	40	25	20
Distilled water	490	390	560	720	830

Table 3: The initial rate and constant of swelling rate of clay-based polymer compositions in chloride nickel solutions at 22°C.

Concentration of chloride nickel, M	Initial rate, g/hour	Constant of swelling rate, min^{-1}
10^{-5}	113.1	0.203
10^{-4}	156.6	0.231
10^{-3}	172.4	0.243
10^{-2}	184.5	0.264
Distilled water	99.3	0.184

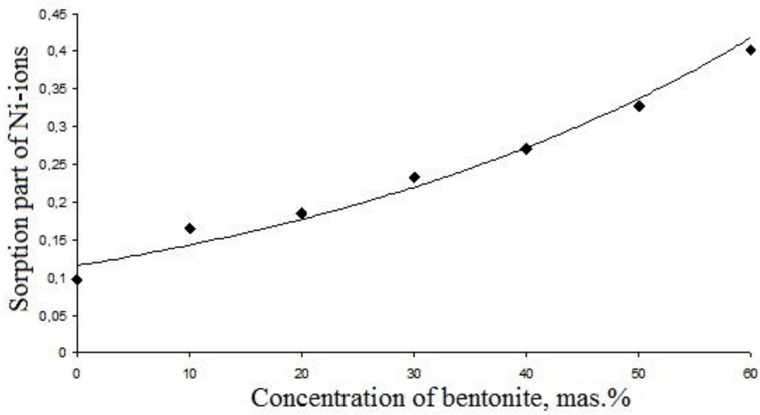

Figure 3: Dependence sorption part of Ni ions on bentonite concentration in clay-based polymer composite in solution of nickel chloride of 10^{-3} mol/L, temperature – 22°C.

4 CONCLUSION

The study involved the investigation of clay-based acrylic superabsorbents synthesized by radical polymerization. The swelling behaviour of polymer nanocomposites was revealed out. Polymer nanocomposites demonstrated a higher swelling degree in distilled water. Studies and the analysis of absorption processes of nickel ions from aqueous solutions showed that the clay-based polymer nanocomposite has high degree of affinity with of heavy metal ions. The bentonite-containing acrylic nanocomposites were used as an absorbent for the removal of polyvalent ions from aqueous solution.

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