

XANTHATE REMOVAL FROM WASTEWATER BY USING SILVER NANOPARTICLES – ZEOLITE COMPOSITE

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Abstract

Water from tailing ponds of mineral processing plants can be discharged to natural water bodies if the concentration of xanthates is below 1 mg/L. The paper presents the removal of potassium ethyl xanthate from model wastewater by silver nanoparticles-zeolite composite. The impact of adsorbent dose, initial pH value of polluted water and initial pollutant's concentration was investigated. The process kinetics is fast. The kinetics of the xanthate immobilization is best described by the pseudo second order model and the equilibrium - by the Langmuir adsorption isotherm. The material exhibits high capacity with respect to the pollutant when the latter is spiked into natural waters. Even more, over 75 % of the pollutant present in clarified real wastewater from zinc-lead ore flotation experiment have been removed in 120 min at adsorbent dose of 0.2 g/L.

Keywords: silver nanoparticles-zeolite composite, xanthate, wastewater

1. INTRODUCTION

Xanthates are widely-used collector compounds in the flotation of sulfide ores. Most of the xanthate is consumed in the flotation process; however some residue amounts remain in the enterprises' wastewater [1]. Xanthates are also used to control radical polymerization and thus they are applied as additives in the curing and vulcanization of rubber and as high-pressure lubricant additives [2]. Xanthates are also commonly used to manufacture cellulose film (cellophane) and rayon. They are also deployed as defoliants, herbicides, insecticides and fungicides in agricultural production [3]. Some antiviral medicines can be prepared based on xanthates [4]. The above mentioned and other industrial applications can lead to a release of water polluted with xanthates into the surrounding surface waters. This is the most common route of exposure for aquatic plants, invertebrates and fish. Under ambient environmental conditions, the half-life of xanthate is approximately four days. Xanthates are toxic to aquatic biota at concentrations of less than 1.5 mg/L [5, 6]. Giving this fact, the waste streams bearing residual xanthates should not be discharged to natural water-bodies without additional treatment.

Different methods have been proposed for xanthate removal from wastewater. Fenton reagent was applied in the degradation experiments of residual xanthate in flotation wastewater. The xanthate removal was 99.5 % (of the initial concentration of 125 mg/L) at initial pH 4, concentrations of reagents: Fe^{2+} - 20 mg/L and H_2O_2 - 20 mg/L and treatment time of 60 min [7]. Beneficiation wastewater containing butyl xanthate was treated by oxidation with sodium hypochlorite. The removal rate of 99.05 % was achieved in 50 min at initial pH 4 and sodium hypochlorite 120 mg/L [8]. A combined use of ultrasound and Fenton reagent was studied to deal with the artificial and real mineral processing wastewater. The removal efficiency is higher than when ultrasound and Fenton reagent are used individually. Removal efficiency of 96.8 % was achieved for simulated wastewater at initial xanthate concentration of 120 mg/L, initial pH 4, and concentrations of reagents: H_2O_2 - 20 mg/L and Fe^{2+} - 12 mg/L. Removal efficiency of 97.6 % was achieved for real wastewater at initial pH 3, and concentrations of reagents: H_2O_2 - 24 mg/L and Fe^{2+} - 18 mg/L [9]. The elimination of butyl xanthate by catalytic ozonation process using Mn-Ce- Al_2O_3 catalyst was studied. The removal ratio of 98.72 % was achieved at initial pH = 7.22, 1.75 g/h of ozone dosage, 0.5 g/L of catalyst loading, 100 mg/L of initial butyl xanthate concentration, and reaction time of 8 min [10].

Application of oxidative and corrosive chemicals, such as Fenton reagent, sodium hypochlorite, hydrogen peroxide, and ozone, requires careful and proper handling and the corresponding equipment. Sorption is considered an environmentally friendly and relatively cheap method for water treatment. Combination of adsorption on materials containing approximately 48% clinoptilolite and 30% mordenite and subsequent dissolved air flotation was proposed for removing isopropyl xanthate from water [11]. The zeolite was preliminary converted to homoionic form by contacting it with NaCl solution. Modified bentonite adsorbents were synthesized and used for the removal of the residual potassium amyl xanthate from the synthetic solutions at adsorbent dosage 7500 mg/L, xanthate concentration 2000 mg/L, pH=12.2, 45 min [12]. Under optimum conditions Al-modified bentonite immobilized 99% of the residual xanthate.

However, xanthate removal, when it is present in relatively low concentrations and at neutral to slightly alkaline pH of the fluid subjected to the treatment, still needs further optimization.

Silver nanoparticles (AgNPs) have attracted the interest of scientists due to their unique properties. They have been studied for different environmental applications, such as water disinfection, removal of pollutants from water, etc. Those applications require stable and non-aggregable nanoparticles. In order to improve AgNPs stability and make them more accessible they can be directly produced and immobilized onto a support, such as natural zeolite, thus forming a nanocomposite material. This makes their application in environmental protection more convenient, long-lasting and cost effective.

In this paper we present results from a study on the capability of the new synthesized AgNPs-natural zeolite composite to immobilize potassium ethyl xanthate from model and real wastewater.

2. MATERIALS AND METHODS

2.1. Preparation and characterization of AgNPs-clinoptilolite composite

Zeolitic rock from East Rhodopes region of Bulgaria was used in the study. After milling and sieving, the fraction 0.09-0.325 mm was deployed. The material was washed, dried and subjected to classical silicate analysis to find its chemical composition that was (in wt. %): SiO₂ – 70.19, Al₂O₃ – 10.90, CaO – 2.87, MgO – 0.51, K₂O – 3.41, Na₂O – 0.36, Fe₂O₃ – 0.28, MnO – 0.04, TiO – 0.06, P₂O₃ < 0.05, SO₃ < 0.05, LOI – 10.99. The theoretical cation exchange capacity of the material was 211 meq/100 g zeolite. The XRD analysis of the washed material has revealed that it contains 73 % clinoptilolite.

Silver ions (Ag⁺) were loaded on the zeolite by placing it in contact with 0.05 M AgNO₃ solution at solid to liquid ratio = 1 : 40 for 4 hours. Ag-loaded zeolite (75 mg Ag/g zeolite) was washed with distilled water till negative reaction for Ag⁺ in washings was observed. Then it was dried at 50 °C overnight. All experiments were carried out under dark conditions, thus taking into account silver light sensitivity. Samples of the Ag-loaded zeolite were heated at 400 °C under air conditions for 2 hours to obtain AgNPs-clinoptilolite composite.

The specific surface area of AgNPs-composite, measured by applying the Brunauer, Emmett and Teller (BET) method and using Quantachrome NOVA 1200e Analyzer working with N₂ was S_{BET} = 16 m²/g. EDS elemental mapping (carried out with JEOL - JSM-6010PLIS/LA) showed that silver is uniformly distributed in the zeolitic material and it presents in amount of around 11 wt. % Ag on the surface of the sample. TEM analysis of prepared composite (carried out on JEOL, model JEM 2100, 200 kV analytical electron microscope) indicated that AgNPs with diameter in the range of 20-25 nm were observed on the material's surface and particles with diameter in the range of 3-5 nm were situated in the zeolite secondary pores. Details on the preparation of the Ag-loaded zeolite and the composite, as well as on composite characterization, can be found in our previous work [13,14] .

2.2. Adsorption experiments

Solutions containing different concentrations of potassium ethyl xanthate (C₃H₅KOS₂) were prepared by dissolving C₃H₅KOS₂ (p.a. – Acros organics) in distilled water. In addition, corresponding amount of solution containing 1 g/L C₃H₅KOS₂ was spiked in three types of natural water with composition

presented in Table 1 in order to obtain xanthate concentration of 20 mg/L. Additionally, an experiment was carried out with wastewater obtained from flotation laboratory experiment with zinc-lead ore, after the wastewater treatment with lime (in “classical method”) and its clarification - this water sample is referred to as “real wastewater”. This water contained Zn - 16 mg/L, Pb 1 mg/L, and Cu - 1 mg/L, as determined by an ICP-OES analysis. In experiments aimed at studying the influence of the adsorbent dose different amounts of AgNPs-composite were added to 200 mL of solution containing 20 mg C₃H₅KOS₂ per liter, considering the concentration of C₃H₅KOS₂ in wastewater released by flotation [1]. The solutions pH was 7.1. To study the influence of the initial water pH value additional experiments were conducted with solutions containing 20 mg C₃H₅KOS₂ per liter at initial pH values of 8.3 and 9.7 (achieved by dropwise addition of 2 M NaOH solution) and 0.2 g AgNPs-composite per liter. The impact of the initial pollutant's concentration was studied at different concentrations of C₃H₅KOS₂ (10, 20, 30, 40 and 60 mg/L) and predetermined conditions (pH 7 and 0.2 g AgNPs-composite per liter).

Table 1. Main parameters of natural water samples spiked with potassium ethyl xanthate and of real wastewater

Water sample No	Water 1	Water 2	Water 3	Real waste water (water 4)
Water parameter				
Ca ²⁺ , mg/L	11,58	5.01	73.1	69.5
Mg ²⁺ , mg/L	3.6	2.4	8.2	3.7
Na ⁺ , mg/L	90.26	49.95	26.2	31.4
K ⁺ , mg/L	0.69	1.93	3.3	1.5
HCO ₃ ⁻ , mg/L	115.93	67.12	237	82.1
CO ₃ ²⁻ , mg/L	6.00	18.00	-	-
SO ₄ ²⁻ , mg/L	109.05	23.66	66	77.2
Cl ⁻ , mg/L	12.41	7.80	7.2	8.7
NO ₃ ⁻ , mg/L	-	1.5	-	-
F ⁻ , mg/L	0.48	4.81	0.48	-
H ₂ SiO ₃ , mg/L	-	45.69	-	-
M, mg/L	387	234	436	
pH	8.33	8.51	7.23	7.8
Water type	Sulfate - hydrogen carbonate - sodium	hydrogen carbonate - carbonate-sodium	hydrogen carbonate - sulfate-calcium-sodium	sulfate - hydrogen carbonate - calcium - sodium

All experiments were conducted batch-wise. The solutions were stirred with magnetic stirrer. Aliquot portions were taken at particular time (5, 10, 15, 30, 45, 60, 90, and where it was needed - 120, 150, 180 min) and the amount of xanthate remained in the solution was determined by UV spectrometry. Absorption at 301 nm, where aqueous solutions of xanthate have an absorbance maximum, and corresponding preliminary prepared calibration line was used.

2.3. Equations used

The pollutant removal from the initial solution, was calculated using the equation (1):

$$\text{Removal, \%} = [(C_0 - C_t) / C_0] \times 100 \quad (1)$$

where C_0 is the initial and C_t is the pollutant concentration (mg/L) at time t (min).

The quantity of immobilized pollutant q_t (mg/g) is calculated according to equation (2):

$$q_t = (C_0 - C_t) \times V / m \quad (2)$$

where C_0 is the initial concentration and C_t is the residual concentration (mg/L) of the pollutant at time t (min), m is the mass of the adsorbent (g) and V is the volume of the solution, contacting with the adsorbent (L). When equilibrium is reached the relation gives the amount q_e (mg/g) of pollutant immobilized per unit mass of the adsorbent at equilibrium:

$$q_e = (C_0 - C_e) \times V / m \quad (2')$$

and C_e is the residual concentration of the pollutant at equilibrium (mg/L).

Experimental data have been fitted to the equations describing the kinetics of the first and second order irreversible reactions [15]. The following equations in linear form have been used:

For the first order irreversible reactions:

$$\ln C_t = -k \times t + \ln C_0 \quad (3)$$

where C_0 and C_t - initial and at time t reactant concentration, k - rate constant [time^{-1}].

For the second order irreversible reactions:

$$1 / C_t = k \times t + 1 / C_0 \quad (4)$$

where k is the reaction rate constant [concentration $\times \text{time}^{-1}$]; C_0 , C_t and t - as described above.

For the pseudo first order kinetic equation [16] (5):

$$\log (q_e - q_t) = \log q_e - (k / 2.303) \times t \quad (5)$$

where t , q_e and q_t are as described above and k is the rate constant [time^{-1}].

For the pseudo second order (PSO) kinetic equation [16] (6):

$$t / q_t = 1 / (k \times q_e^2) + t / q_e \quad (6)$$

where k is the rate constant of PSO adsorption reaction [concentration $\times \text{time}^{-1}$] and t , q_e and q_t are as described above.

Pseudo first and PSO kinetic equations are macroscopic models usually applied for explaining the adsorption mechanism. The pseudo-first-order kinetic model assumes that physical factors mainly influence the adsorption process. The adsorption kinetics best described by the PSO model is an indication that the chemisorption is the rate-limiting step of the adsorption [17].

Freundlich and Langmuir isotherm equations were tested for their ability to describe the adsorption equilibrium. The isotherms were used in their linear form [18]:

Freundlich equation:

$$\log q_e = \log K_F + 1/n \times \log C_e \quad (7)$$

where q_e and C_e - as described above, K_F - Freundlich constant [$\text{mg}^{(1-1/n)} \times \text{L}^{1/n} / \text{g}$] or given as $[(\text{mg/g}) / (\text{L/mg})^{1/n}]$.

Langmuir equation:

$$C_e / q_e = 1 / (K_L \times q_{\max}) + C_e / q_{\max} \quad (8)$$

where $q_{\max}$ (mg/g) is the maximum adsorption capacity, and K_L is the Langmuir equilibrium constant (L/mg) related to the energy of adsorption, q_e , and C_e - as described above.

3. RESULTS AND DISCUSSION

3.1. Effect of the adsorbent dose

To study the influence of the adsorbent dose different amounts of AgNPs-composite were added to 200 mL of solution containing 20 mg $C_3H_5KOS_2$ per liter. Results from the experiments are presented in Figure 1.

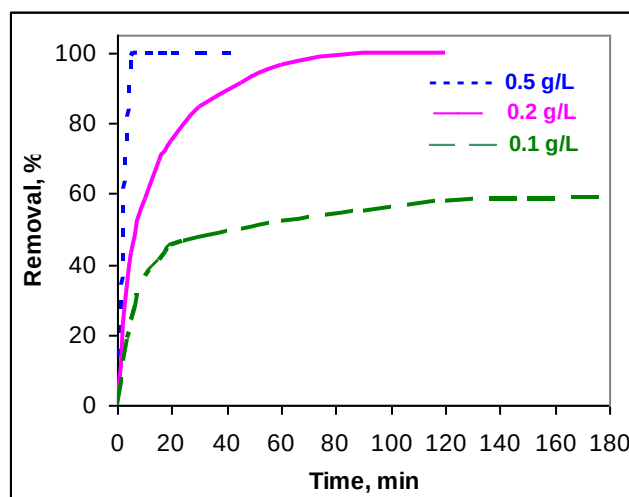


Fig. 1. Potassium ethyl xanthate removal at different adsorbent dose and initial pollutant concentration 20 mg/L

As it can be seen in Figure 1, the amount of adsorbent impacts significantly the process kinetics. Practically, the pollutant is entirely removed in only 10 min at the highest added dose of the composite - 0.5 g/L. The total pollutant removal (final concentration < 0.02 mg/L) was achieved in 90 min at composite dose of 0.2 g/L, while at dose of 0.1 g/L only approximately 60 % of the pollutant were removed for 180 min. In order to achieve a high removal and at the same time to ensure a room for evaluating the impact of the initial pH value of the water and initial pollutant's concentrations, the further studies were carried out at composite dose of 0.2 g/L.

3.2. Effect of the initial pH value

The effect of initial pH was studied in the neutral - alkaline range, due to the following reasons: (a) it is well known that xanthates are unstable in the acidic solutions [3], (b) the natural decomposition of ethyl xanthate in the pH range 7-11 at room temperature is independent of pH [19], and (c) this is the pH of the natural wastewater polluted with xanthates and released by the mineral processing. Xanthate removal in dependence on the water pH is presented in Figure 2.

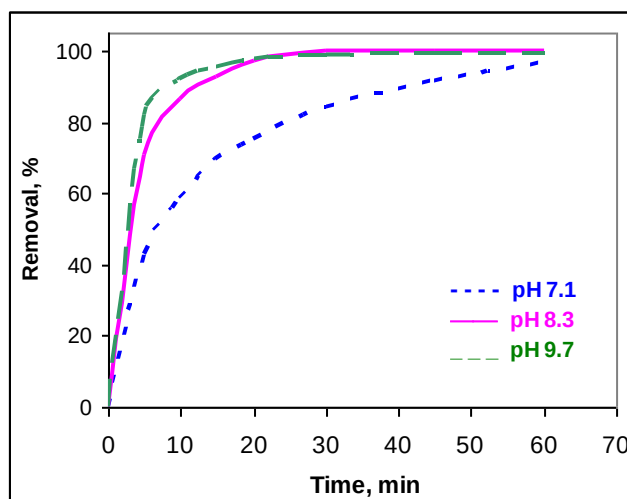


Fig. 2. Potassium ethyl xanthate removal at different initial pH values, initial pollutant concentration 20 mg/L and adsorbent dose 0.2 g/L

As it can be seen in Figure 2, an increase in the initial pH value of the polluted water leads to faster xanthate removal. This could be attributed to the higher degree of dissociation of potassium xanthate at the higher pH value. Since as mentioned above, in the studied pH range the natural decomposition of xanthate in the pH range 7-11 at room temperature is independent of pH, our findings could be related to the facilitated chemisorption of xanthate on the composite at higher pH values (see also sections 3.4 and 3.5). In addition, it has been found that the natural decomposition of water solutions of xanthate follows the first order kinetics [3, 19] while in our case the xanthate removal is best described by the PSO equation. This finding supports the suggestion that the influence of the initial pH value on the xanthate removal is not related to the xanthate natural decomposition.

3.3. Effect of the initial pollutant concentration

The impact of the initial pollutant's concentration has been studied at concentrations 10, 20, 30, 40 and 60 mg/L. Results are presented in Figure 3.

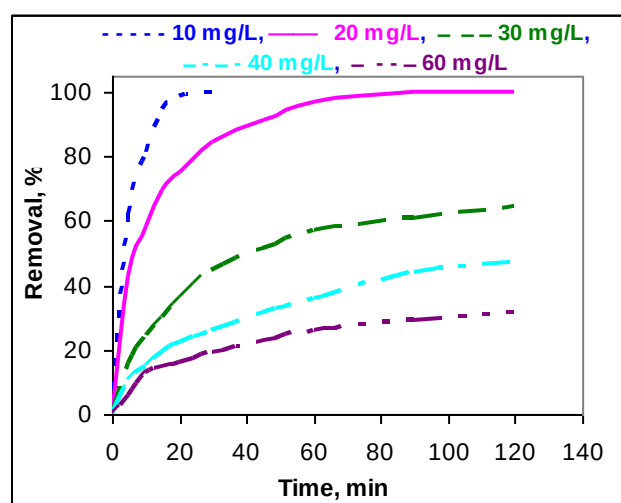


Fig. 3. Potassium ethyl xanthate removal at different initial pollutant concentration and adsorbent dose 0.2 g/L

As it can be seen in Figure 3, practically 100 % removal is achieved at initial concentrations of 10 and 20 mg/L. Further increase in the initial pollutant concentration leads to a decrease in the removal. However, the absolute removed amount of xanthate at equilibrium is practically the same for concentrations equal or higher than 20 mg/L. This could be related to a saturation of the available adsorption sites of composite.

3.4. Adsorption isotherm

It has been found that the process is well described by the Langmuir isotherm - Figure 4.

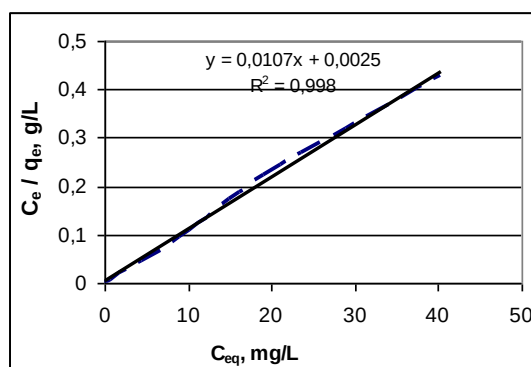


Fig. 4. The Langmuir isotherm model fitting: adsorbent dose 0.2 g/L, 22 °C

The Langmuir isotherm assumes mono-layer coverage on the adsorbent with uniform surface with a finite number of equivalent adsorption sites that are saturable. Maximum capacity of adsorption is achieved when all the sites are saturated with adsorbates. Generally, it describes chemisorption [18].

In addition, a fundamental parameter of the Langmuir model can be represented by a dimensionless constant, R_L , which is determined by the equation (9) :

$$R_L = 1 / (1 + K_L \times C_0) \quad (9)$$

where K_L is the Langmuir constant (L/mg) and C_0 is the initial concentration (mg/L) of adsorbate in solution. The adsorption is: (i) favorable when $0 < R_L < 1$; (ii) unfavorable if $R_L > 1$; (iii) linear at $R_L=1$; and (iv) irreversible at $R_L=0$.

In our case the calculated maximum adsorption capacity is 93.46 mg/g, and $0 < R_L < 1$ - showing a favorable process.

3.5. Adsorption kinetics

The experimental data presented in Figure 3 have been fitted to the kinetic equations (3) - (6). It has been found that the xanthate removal is best described by the PSO kinetic equation, for which the coefficients of determination (R-squared) was the highest - Table 2.

Table 2. The R^2 value for the studied kinetic models of xanthate removal from model wastewater

Initial concentration, mg/L; Reaction order	10	20	30	40	60
First	0.9730	0.9912	0.8704	0.9304	0.8547
Second	0.6410	0.5873	0.9442	0.9691	0.8920
Pseudo-first	0.9672	0.9921	0.9945	0.9664	0.9929
Pseudo-second	0.9985	0.9997	0.9990	0.9754	0.9932

Generally kinetics description by the pseudo-second-order equation indicates that the rate-limiting step of adsorption is the chemisorption [17]. Chemisorption of xanthate on silver admixtures in gold-bearing ores is well documented [20]. The very pronounced dependence of the xanthate removal on the AgNPs-composite dose, as well as practically the same amounts removed at the same composite dose at different initial pollutant's concentration also support the suggestion that the xanthate chemisorption is the rate determining stage of the xanthate removing process.

3.6. Effect of the different water matrices

It is known that different ions presenting in water can change or modify the processes of pollutants removal [21, 22]. Results from studies on the xanthate removal from different types of water are presented in Figure 5.

As it can be seen in Figure 5, the different water matrices do not impact significantly the xanthate removal from natural waters spiked with xanthate. The process is slowed down a little in time but over 96 % removal is achieved in 120 min. Even more, for the water with the highest pH value over 99 % removal is achieved in 120 min which is similar to the case of model water with the near pH value (compare Figures 2 and 5). In the three waters the xanthate concentration after 120 min was < 1 mg/L. It is worth noting that even from real wastewater over 75 % of the pollutant are removed in 120 min.

The experimental data for natural waters were also fitted to the kinetic equations (3) - (6). The data on the coefficients of determination (R-squared) are given in Table 3. As it can be seen from the Table, the xanthate removal is again best described by the PSO kinetic equation. This finding implies that the xanthate removal mechanism is not changed and the chemisorption is again the rate determining stage of the removing process.

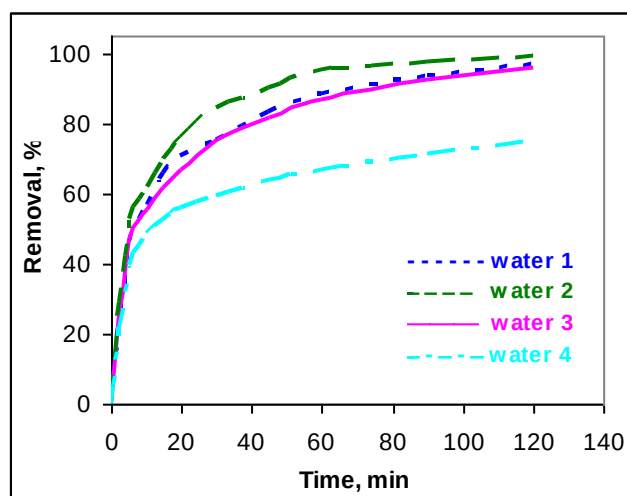


Fig. 5. Potassium ethyl xanthate removal from different water matrices and initial pollutant concentration of 20 mg/L (23.7 mg/L for the real wastewater) and adsorbent dose 0.2 g/L

Table 3. The R^2 value for the studied kinetic models of xanthate removal from natural water spiked with xanthate and from real wastewater

Initial concentration, mg/L; Reaction order	Water 1	Water 2	Water 3	Real wastewater (water 4)
First	0.9584	0.9496	0.9579	0.7124
Second	0.8928	0.7326	0.9205	0.8707
Pseudo-first	0.9952	0.9315	0.9970	0.9908
Pseudo-second	0.9986	0.9993	0.9980	0.9984

4. CONCLUSIONS

Based on the studies carried out the following conclusions can be drawn:

1. AgNPs-clinoptilolite composite is a suitable material for removing xanthates from the wastewater in concentrations typical of clarified wastewater from mineral processing industry. Starting from 20 mg/L, concentrations lower than 1 mg/L can be achieved in 60 min at initial pH 7 of polluted model wastewater. In the initial pH range 8 - 10 the process is faster and concentration lower than 1 mg/L is achieved in 20 min.
2. AgNPs-clinoptilolite composite removes xanthate at initial concentration 20 mg/L from different natural waters spiked with the pollutant. A concentration lower than 1 mg/L is achieved in 120 min.
3. The prepared composite removes over 75 % of the xanthate present in clarified wastewater from flotation of zinc-lead ore in 120 min. For example, concentration of 5.8 mg/L was reached starting from 23.7 mg/L.
4. Under all studied conditions, the kinetics of the uptake process is best described by the equation of pseudo second order reactions. The data obtained are best fitted to the Langmuir adsorption isotherm. The calculated maximum adsorption capacity is 93.46 mg/g and the process is favorable. Findings for the adsorption kinetics and isotherm imply that the xanthate chemisorption is the rate determining stage of the xanthate removing process.

ACKNOWLEDGEMENTS

The authors thank the National Science Fund of Bulgaria for the financial support of the project DN-17/20.

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