STUDIA UBB CHEMIA, LVI, 1, 2011

ORGANICS REMOVAL FROM AQUEOUS SOLUTIONS USING SUSPENDED AND IMMOBILIZED ROMANIAN BENTONITES

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ABSTRACT. This work presents experimental results obtained in the process of phenol and Fastac pesticide removal from aqueous solutions using batch technique (immobile phases, 3D shaker, magnetic stirring) on Romanian bentonites (Oraşul Nou and Petreşti deposits). Bentonite samples were used in suspension and immobilized in alginate beads. Influences of bentonite provenience and quantity, batch contact type and phenol concentration over the process efficiency were studied. The most effective bentonite proved to be the one from Oraşul Nou. Removal efficiencies up to 80% were reached in case of phenol solutions with concentrations smaller then 50 mg/L on immobilized bentonite and Fastac (100 mg/L) on suspended bentonite. Also, adsorption capacity increased with the decrease of the bentonite quantity and the increase of the initial phenol concentration.

Keywords: *bentonite, suspension, alginate beads, phenol, pesticide, adsorption*

INTRODUCTION

Phenolic compounds, which are released into the aquatic environment by industries such as coke ovens in steel plants, petroleum refineries, petrochemical, phenolic resin, and fertilizer, pharmaceutical, chemical, and dye industries and have been reported in hazardous wastes sites, are considered to be hazardous wastes [1].

The utilization of phenol-contaminated waters causes protein degeneration, tissue erosion, paralysis of the central nervous system and also damages the kidney, liver and pancreas in human bodies [2].

According to the recommendation of World Health Organization (WHO), the permissible concentration of phenolic contents in potable waters is 1g/L [3] and the regulations by the Environmental Protection Agency (EPA), call for lowering phenol content in wastewaters less than 1mg /L [4].

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According to Romanian legislation the maximum allowable concentration of phenol in surface waters and municipal sewer system is 0.3 and 30 mg/L, respectively [5], therefore elimination of phenol becomes a necessity in order to preserve water quality [6]. In case of drinking water Romanian legislation states values of 0.001 to 0.1 mg phenol/L for waters that are used for drinking water production [5].

Fastac is one of the many commercial names for alpha-cypermethrin, which is a compound from synthesis pyrethroid pesticide group. It is used on a large scale as an insecticide and acaricide. It behaves as neurotoxin (non-systemic insecticide) in insects (e.g. cockroaches, mosquitoes, flies). Alpha-cypermethrin is highly toxic to fish, bees and aquatic insects; it can produce acute poisoning in humans (tingling, burning dizziness, itching, nausea, tiredness) by contact inhalation or ingestion [7]. According to Romanian legislation the maximum allowable concentration of pesticide as total pesticides varies from 0.5 μg/L for potable water to 1-5 μg/L for waters subjected to various treatments in order to obtain potable water [5].

Various methods have been proposed for the treatment of wastewaters containing organic and inorganic pollutants. These processes are based on the principles of precipitation and coagulation, chemical oxidation, sedimentation, filtration, adsorption, osmosis, ion exchange, etc. Adsorption technology is currently being used extensively for the removal of organic and inorganic micro pollutants from aqueous solutions. There are many absorbents in use. Activated carbon is the most widely used for the removal of a variety of organics from waters, but the disadvantage associated with it is the high regeneration cost and the generation of carbons fines, due to the brittle nature of carbons used for the removal of organic species [8].

Adsorbents from low-cost materials, such as fertilizer wastes [9], wood [10], and rice husk [11], by several chemical treatments are currently developed for phenol removal. The use of sawdust for the removal of phenol from aqueous solution was also studied by Sivanandam and Anirudhan [12].

Natural zeolites gained a significant interest among scientist, mainly due to their valuable properties such as ion exchange ability and high surface areas. Large deposits of natural zeolites in many countries such as Greece, UK, Italy, Mexico, Iran, and Jordan, provide local industries some promising benefits such as cost efficiency since they are able to treat wastewater contaminated with organic solutes at low-costs [8,13].

Clay is one of the potential alternatives to activated carbon as well. Similar to zeolites, clay minerals are important inorganic components in soil. Their sorption capabilities come from high surface area and exchange capacities. The negative charge on the structure of clay minerals gives clay the capability to be modified by surfactant. USA, Lithuania, Georgia, Romania and Kazakhstan are well known for their large deposits of natural clay minerals [6,8,14].

Bentonite is a member of 2:1 clay minerals (meaning that it has two tetrahedral sheets sandwiching a central octahedral sheet) which consists essentially of clay minerals of montmorillonite group. Bentonite is characterized by an Al octahedral sheet between two Si tetrahedral sheets. It has a negative surface charge created by the isomorphous substitution of Al^{3+} for Si^{4+} in tetrahedral layer and Mg^{2+} for Al^{3+} in octahedral layer. The bentonite surface is hydrophilic in nature because inorganic cations, such as Na^+ and Ca^{2+}, are strongly hydrated in presence of water. As a result, the adsorption efficiency of natural bentonite for organic molecules is low. The adsorption properties of bentonite can be improved by the modification of clay mineral surface with a cationic surfactant. [15,16].

The aim of this work was to investigate, the potential of two Romanian bentonites from Oraşul Nou, (ON), Satu Mare County, and Petreşti (P), Cluj County, used in suspension, and immobilized in calcium alginate to adsorb phenol and Fastac pesticide from aqueous solutions, in batch conditions (Influences of bentonite provenience and quantity, batch contact type and phenol concentration over the process efficiency were studied). The considered bentonites were used without any chemical modification of their structure.

RESULTS AND DISCUSSION

Bentonite samples

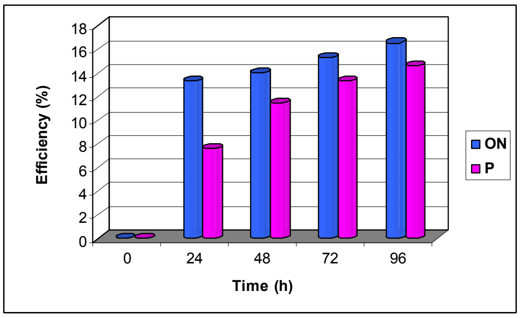
In order to realise the proposed adsorption study, two bentonite samples were collected from two deposits located in Transylvania, Romania, namely, Oraşul Nou, (ON), and Petreşti (P). Bentonite samples were collected as representative bulk rock sample from the open pits.

The bentonite deposit from Oraşul Nou (Satu Mare County) is located about 30 km north-west of the city of Baia Mare. The bentonites were formed by alteration of rhyolites and perlites, due to the solutions' complex circulation through the rocks. They are white in colour, fine grained or compact, the perlitic fabric being more or less preserved. The mineralogical composition of raw material was analysed using XRD and indicates the presence of montmorillonite, as the main clay mineral (subordinately kaolinite, illite), cristobalite, carbonates, clinoptilolite, iron oxi-hydroxides and quartz and feldspar (as relics of primary minerals). According to the transformation degree of the primary rock, the amount of montmorillonite varies between 20-85% [17].

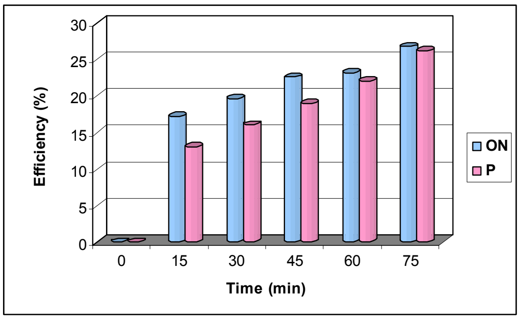
The bentonite deposit from Petreşti (Cluj County, Romania) is located at about 30 km south from Cluj-Napoca (north-western part of Romania). The bentonite deposit was formed at then contact of the carbonate rocks (Upper Jurassic age) and basaltic andesites and basalts rock, generated by circulating hydrothermal fluids. The main rocks are represented by Ca-bentonites white and white-yellowish in color. Mineralogical composition of clay raw material resulting from X-ray diffraction analyses is represented by smectite (montmorillonite) 65-72%, mica/illite, quartz, cristobalite, feldspars and clinoptilolite [14].

Suspended bentonite – phenol removal

In figure 1 are presented the results obtained for the two bentonite samples in batch conditions, immobile phases and magnetic stirring. It can be observed that the highest increase of the removal efficiency is in the first 24 hours, respectively in the first 15 minutes from the beginning of the experiment depending on the contact type (immobile vs. stirring).



(a).



(b).

Figure 1. Time evolution of phenol removal efficiency on bentonite samples (suspended) from Oraşul Nou (ON) and Petreşti (P) in batch conditions, solid : liquid ratio = 1:10, C_i = 100 mg phenol/L; (a) immobile phases, and (b) magnetic stirring.

Also the equilibrium was reached after 96 hours, respectively after 75 minutes (diffusion limitations are reduced with stirring intensification) for both bentonite samples. If we compare the values obtained for ON and P samples it is easy to observe that in all cases the ON sample proved to be more efficient, results that can be correlated with the specific surface area of the bentonite sample, which is higher in case of ON (72 m^2/g) by comparison with 64 m^2/g for P.

In case of the batch conditions realised using a 3D shaker, exemplified for P sample in figure 2, equilibrium was reached after 150 minutes suggesting that external diffusion limitation are diminished by comparison with immobile phases, but they still have a great influence taking in account that the equilibrium was reached in 150 minutes by comparison to 75 minutes for the magnetic stirring. Another aspect observed in case of 3D shaker by comparison with magnetic stirring was that the increase of the adsorption efficiency (decrease of the phenol quantity in solution) takes place more slowly.

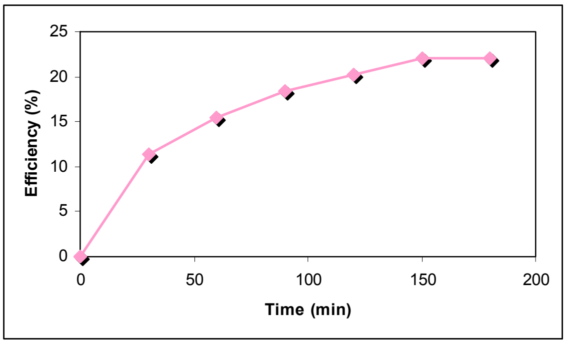


Figure 2. Time evolution of phenol removal efficiency on bentonite sample (suspended) from Petreşti (P) in batch conditions – 3D shaker, solid : liquid ratio = 1:10, C_i = 100 mg phenol/L.

The influence of the contact type in batch conditions for phenol adsorption in suspension is presented in figure 3, for ON sample. As the intensity of the mass transfer increases due to a more intense stirring, the removal efficiency also increases.

The influence of the bentonite quantity (solid : liquid ratio) over the removal process efficiency is exemplified in figure 4, for P sample when 2 and 4 grams of bentonite were suspended in 20 ml of phenol solution. An increase in the adsorbent quantity led to only a small increase in the removal efficiency, suggesting that an increase of the bentonite quantity (more than 2 grams) is not economically feasible.

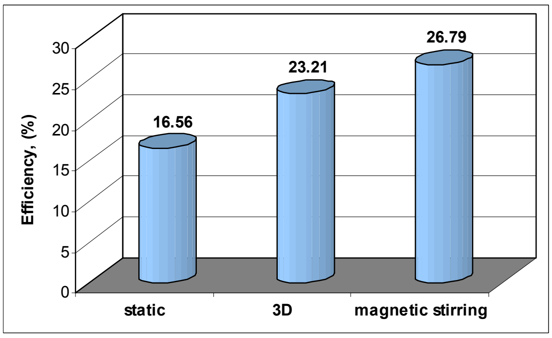


Figure 3. Maximum phenol removal efficiency on ON bentonite sample (suspended), obtained in batch conditions, solid : liquid ratio = 1:10, C_i = 100 mg phenol/L.

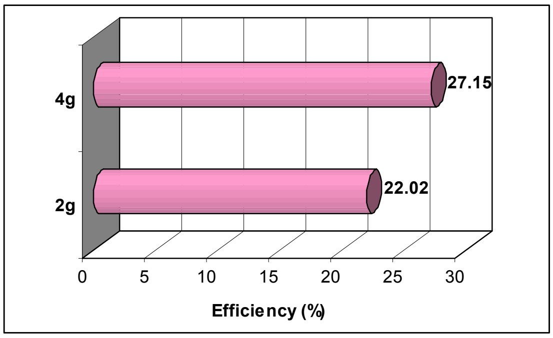


Figure 4. Bentonite quantity influence over the maximum phenol removal efficiency on the P bentonite sample (suspended) in batch conditions – 3D shaker, corresponding to a solid : liquid ratio of 1:10 and 2:10 respectively, C_i = 100 mg phenol/L.

Suspended bentonite – Fastac (alpha-cypermethrin) removal

Adsorption of Fastac pesticide was realised in similar conditions on the ON and P samples. In case of immobile phases (static), as for phenol, the adsorption equilibrium was reached in 96 hours, again with better removal efficiencies on the ON sample, 65.78% (ON) by comparison with 57.22% (P). In case of magnetic stirring, figure 5, adsorption efficiency increased very much in the first 15 minutes, after that a slowly increase until equilibrium (75 minutes) being observed. A direct comparison between the batch conditions, figure 6, showed that magnetic stirring is more efficient due to a more intense stirring leading to a more intense mass transfer. The highest adsorption efficiency was calculated to be 78.61% in case of ON bentonite sample.

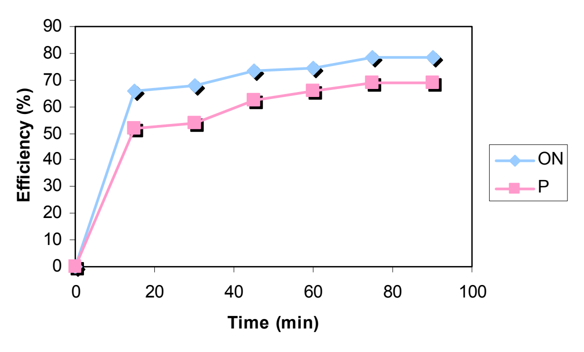


Figure 5. Time evolution of Fastac removal efficiency on bentonite samples (suspended from Oraşul Nou (ON) and Petreşti (P) in batch conditions – magnetic stirring, solid : liquid ratio = 1:10, C_i = 100 mg Fastac/L.

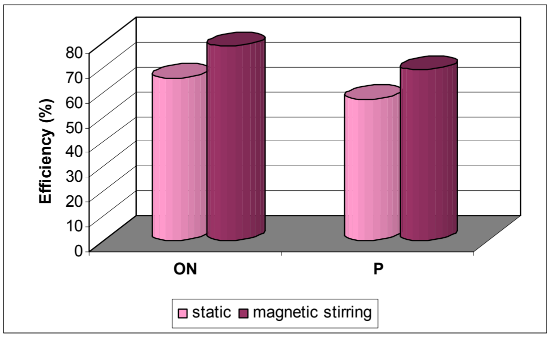


Figure 6. Maximum Fastac removal efficiencies on Oraşul Nou (ON) and Petreşti (P) bentonite samples (suspended), obtained in batch conditions, solid : liquid ratio = 1:10, C_i = 100 mg Fastac/L.

Immobilized bentonite – phenol removal

In the first stage of the experiment, phenol adsorption was realised in a batch reactor with mobile phases, benonite-alginate beads, ON and P samples, being contacted with the phenol solution using a magnetic stirrer. The obtained results are presented in terms of adsorption capacity evolution in time, figure 7, and maximum adsorption efficiency, figure 8, for the same quantity of bentonite present in the beads (8g) and the same phenol initial concentration (103.77 mg/L). From figure 7 it can be observed that in the first 15 minutes from the beginning of the experiment the highest quantity of phenol is removed. Also at the beginning of the experiment P sample looks to be more efficient, while towards the end of the experiment ON sample will retain a higher quantity of phenol. This fact can be attributed to the internal diffusion limitation for ON sample which has a higher specific surface area as was mentioned before. Adsorption capacity was calculated to be 0.708 mg/g and 0.629 mg/g for ON and P samples respectively. The adsorption equilibrium was reached after 180 minutes. If we compare this value with that obtained when the bentonite was suspended (75 minutes) it can be observed that the time for reaching equilibrium is more than double (due to diffusion limitation in the alginate bead). Maximum values for adsorption efficiencies, figure 8, showed also that ON immobilized bentonite sample is more efficient in phenol removal process. Taking into account the fact that ON bentonite sample proved to be the most efficient one in the phenol adsorption process, this sample was next considered for the rest of adsorption experiments.

For a better use of the adsorbent (optimisation of the adsorbent quantity) the next stage of the experiment was to study the evolution of the adsorption process for different ON bentonite quantities immobilized in calcium alginate beads (2-8g) at different initial concentrations of phenol in solution. In figures 9 and 10 the results obtained for C_i = 157.23 mg phenol/L and all considered bentonite quantities are presented. Evolution of the adsorption efficiency in time, figure 9, showed that in the first 15 minutes from the beginning of the experiment, the highest quantity of phenol was adsorbed, after that the adsorbed quantity increase very slowly in case of 2 and 4 g of bentonite and increase slowly in case of 8g benotnite. Equilibrium was reached in about 60 minutes.

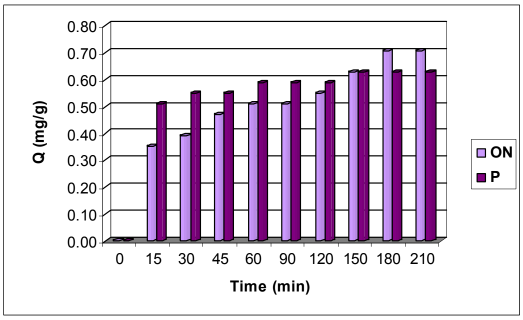


Figure 7. Time evolution of phenol adsorption capacities for Oraşul Nou (ON) and Petreşti (P) bentonite samples (immobilized), 8g bentonite, C_i = 103.77 mg phenol/L.

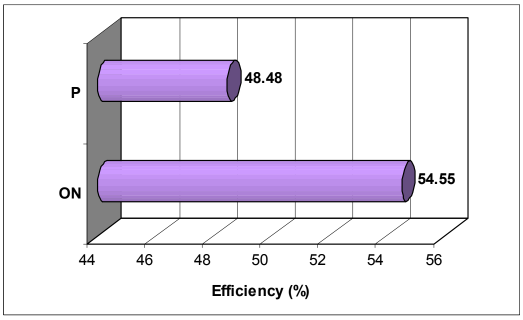


Figure 8. Maximum adsorption efficiency obtained on bentonite samples (immobilized) from Oraşul Nou (ON) and Petreşti (P), 8g bentonite, C_i = 103.77 mg phenol/L.

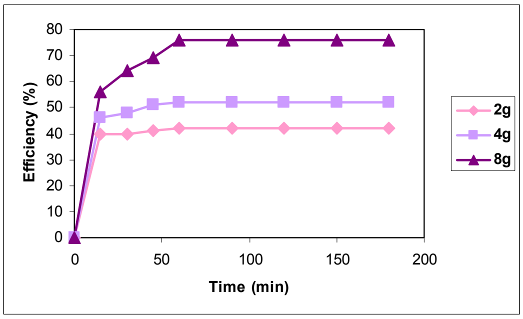


Figure 9. Influence of the bentonite quantity over the time evolution of phenol removal efficiency, 4g ON bentonite (immobilized), C_i = 157.23 mg phenol/L.

To have a more complete image of the adsorption process on the chosen bentonite sample, adsorption capacities were calculated in order to include into the numerical values also the bentonite quantities we used, figure 10. From the values in figure 10, it is easy to observe that as the bentonite quantity increases, the adsorption capacity decreases. Therefore if an adsorption process of this type is considered for practical uses, it will be necessary to take into consideration the initial phenol concentration and water quantity that need to be treated, in order to establish the appropriate bentonite quantity. Also adsorption efficiency should be calculated and evaluated along with bentonite quantity from the economic point of view. As our results show, an increase of the bentonite quantity will lead to an increase of adsorption efficiency, which will finally lead to an increase of the operating cost.

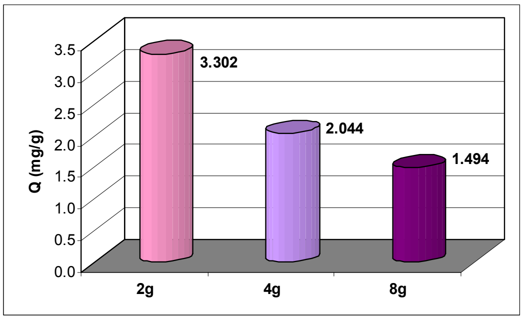


Figure 10. Bentonite quantity influence over the adsorption capacity values for phenol removal, ON bentonite (immobilized), C_i = 157.23 mg phenol/L.

In the final part of the study, the influence of the initial phenol concentration over the adsorption process was studied. Were used solutions containing between 31 and 160 mg phenol/L and as adsorbent 4g of ON bentonite immobilized in calcium alginate beads. Influence of phenol initial concentration over the evolution of phenol concentration in time is presented in figure 11.

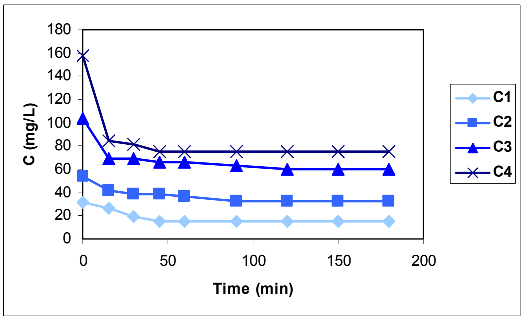


Figure 11. Influence of the phenol initial concentration over the removal process kinetics on 4g ON bentonite (immobilized), C_1 = 31.35, C_2 = 53.46, C_3 = 103.77, C_4 = 157.23 mg phenol/L.

As the initial concentration decreases, the quantity of phenol retained in the first 15 minutes decreases also, due to the smaller difference that exist between the concentration of phenol on the adsorbent surface and in the solution. Therefore the adsorption capacity of the immobilized ON, increases with an increase of the phenol initial concentration, from 0.393 to 2.044 mg phenol/L, figure 12.

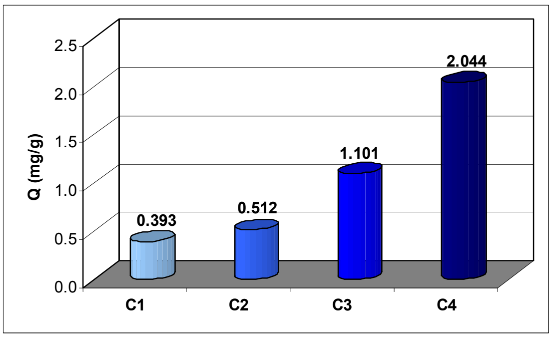


Figure 12. Adsorption capacity values for phenol removal for different initial concentrations, 4g ON bentonite (immobilized), C_1 = 31.35, C_2 = 53.46, C_3 = 103.77, C_4 = 157.23 mg phenol/L.

CONCLUSIONS

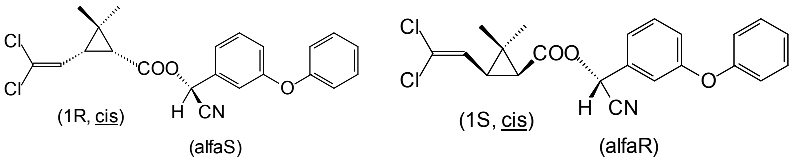
This work presents experimental results obtained in the process of phenol and Fastac pesticide removal from aqueous solutions using batch technique (immobile phases, 3D shaker and magnetic stirring) and suspended and alginate immobilized bentonite as adsorbent. Influences of bentonite provenience (Oraşul Nou and Petreşti samples) and quantity (2-8 grams), batch contact type and phenol concentration (31-160 mg/L) over the process efficiency were studied.

The most effective bentonite sample proved to be the one from Oraşul Nou in suspended and alginate immobilized form as well. Removal efficiencies up to 80% were reached. Also, adsorption capacity increased with a decrease in the bentonite quantity and an increase of the initial phenol concentration showing the capacity of this adsorbent to retain organic compounds.

EXPERIMENTAL SECTION

In this study two bentonite samples collected from two deposits, Oraşul Nou, (ON), Satu Mare County, and Petreşti (P), Cluj County, were used as adsorbents for phenol and Fastac (alpha-cypermethrin). The two bentonite samples were used suspended or immobilized in Ca-alginate beads. The bentonite samples were used as powder, (d < 0.2 mm), without any chemical treatment.

Phenol solutions with concentrations ranging from 31 to 160 mg/L were prepared. Fastac working solution, 100 mg/L, was obtained from commercial available pesticide vials. Fastac is one of the many commercial names for alpha-cypermethrin, which is a compound from synthesis pyrethroid pesticide group, containing more than 90% the most active pair (Scheme 1, (*RS*)-α-ciano-3-fenoxibenzil (1*RS*)-*cis*-3-(2,2-diclorovinil)-2,2-dimetilciclopropan carboxilat) from the 4 cis isomers of cypermethrine, as racemic mixture [7].



Scheme 1

Beside Fastac which was used in its commercial available form, all chemicals used in this study were analytical reagent grade (phenol, alginic acid sodium salt, ethanol and $CaCl_2$).

Removal efficiencies (E, %), equation (1), and adsorption capacities (Q, mg/g), equation (2), were calculated in order to establish the effectiveness of the considered samples in the organics removal process (the calculated values of removal efficiencies and adsorption capacities should be regarded according to the precision of the determination methods we used). Q was calculated just in case of immobilized bentonite where phenol was determined using the spectrophotometric procedure.

$$E = \frac{C_i - C_t}{C_i} \cdot 100 \tag{1}$$

$$Q = \frac{C_i - C_t}{m} \cdot \frac{V}{1000} \tag{2}$$

where,

C_i, initial organic concentration in solution, in mg/dm^3
C_t, organic concentration in solution at time t, in mg/dm^3
V, sample volume, 100 cm^3
m, bentonite quantity, in g.

Suspended bentonite

Bentonite samples were suspended in phenol or Fastac solutions and contacted in three ways in batch conditions: immobile phases (static), mobile phases 3D shaker (GFL 3012) and magnetic stirring (FALC F60, 825 rpm) with a solid liquid ratio of 1:10 and 2:10. In order to determine organics concentration in the aqueous solutions, water samples were collected every 24 hours, every 15 minutes and every 30 minutes for batch conditions realised in static, 3D and magnetic stirring conditions respectively. The experiments were conducted in isothermal conditions at room temperature until equilibrium was reached. Organics concentration in solution was determined as chemical oxygen demand COD, using $KMnO_4$ standard procedure. Prior to this determination a centrifugation procedure at 5000 rpm (Hettich EBA21) was realised in order to remove solid particles from solution. We studied the influence of the bentonite provenience and quantity, and working conditions over the process efficiency.

Immobilized bentonite

ON and P bentonite samples powder were immobilized in alginate beads using the entrapment procedure with calcium alginate [18,19]. Thus, various quantities of bentonite (2, 4, 8, g) were immobilized in Ca-alginate beads. For phenol adsorption study we used aqueous solutions containing between 31 and 160 mg phenol/L. Concentration of phenol in solution was determined using a Jenway 6305 UV/VIS spectrophotometer (UV, 270 nm) after a preliminary centrifugation (14000 rpm, Mikro 200R Hettich centrifuge). Phenol adsorption process was realized in batch conditions under magnetic stirring (FALC F60, 825 rpm) using 100 ml phenol solution of different concentrations, in which Ca-alginate bentonite beads obtained from the desired quantity of adsorbent were suspended. In order to determine the exact concentration of phenol and establish the evolution of the removal process, water samples from the supernatant, diluted as required, were collected at different time intervals, every 24 hours when we used immobile phases, and every 15 minutes for the first hour and next every 30 minutes when we used mobile phases (magnetic stirring), until equilibrium was reached. We studied the influence of the bentonite provenience and quantity, and phenol concentration in solution over the process efficiency in batch conditions.

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