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Dedicated to the memory of Prof. dr. Ioan Silaghi-Dumitrescu marking 60 years from his birth

PHENOL CONTAMINATED WATER REMEDIATION USING COMMERCIAL IMMOBILIZED BENTONITES AS ADSORBENTS

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ABSTRACT. This work presents experimental results obtained in the process of phenol removal from model solutions using batch technique (magnetic stirring, 100 ml solution). As adsorbent we used five commercial bentonites immobilized in calcium alginate beads. Influences of bentonite provenience and quantity (2-10 grams), and phenol concentration (31-160 mg/L) over the process efficiency were studied. The adsorption capacity decreases in order B5 (Fort Benton) > B2 $\cong$ B3 $\geq$ B4 > B1 (BW200). Also, adsorption capacity increased with a decrease in the bentonite quantity and an increase of the initial phenol concentration. Maximum adsorption capacity was calculated to be 2.2013 mg phenol/g.

Keywords: *immobilized bentonite, alginate beads, phenol removal, adsorption*

INTRODUCTION

Water pollution is indeed of great concern since it is a major carrier of both organic and inorganic contaminants [1].

Aromatic compounds are a class of compounds regarded as ubiquitous pollutant. Many aromatic compounds exhibit carcinogenic, teratogenic or mutagenic properties [2].

Phenol is an aromatic compound that is one of common contaminants in wastewaters, being generated from petroleum and petrochemical, coal conversion, and phenol-producing industries [3].

Phenol are extensively used for the commercial production of a wide variety of resins including phenolic resins, which are used as construction materials for automobiles and appliances, epoxy resins and adhesives, and polyamides for various applications [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.

The most common methods used for removal of phenol from industrial effluents include stripping, solvent extraction, chemical oxidation (using O_3, H_2O_2 and ClO_2), incineration, reverse osmosis and irradiation, ion exchange, biodegradation and adsorption methods [6-8]. Out of all these methods, adsorption has been known to be one of the most commonly used treatment methods for removal of phenol from industrial effluents, by virtue of its cost-effectiveness as well as efficiency [9].

Many of water contaminants can be removed by adsorption using natural and synthetic adsorbents. Due to their excellent adsorption properties, clay minerals are widely used in environmental applications. The removal of phenol is a good example for these applications [10].

There are a number of papers in the literature which deals with the removal of phenol by unmodified and modified (acid treated, organobentonites) clays [11-14]. All studies concluded that these types of materials can successfully remove phenol from aqueous solutions, due to their high specific surface area, and their chemical and mechanical stability.

Bentonite consists essentially of clay minerals of the smectite (montmorillonite) group and has a wide range of industrial applications including clarification of edible liquids (wine, for example) and mineral oils, paints, cosmetics and pharmaceuticals.

The abundance of bentonite in most continents of the world and its low cost make it a strong candidate as an adsorbent for the removal of many pollutants and wastewater remediation [3].

The aim of this work was to investigate, experimentally, the potential of five commercial bentonites used as beads (immobilized in calcium alginate) to adsorb phenol from aqueous solutions, in batch conditions.

RESULTS AND DISCUSSION

Bentonite provenience

In the first stage of the experiment, phenol adsorption was realised in a batch reactor with immobile phases using all five bentonites immobilized in calcium alginate beads. This experiment was performed in order to choose between the available bentonites the most effective one to continue the phenol adsorption study. The obtained results are presented in terms of phenol concentration evolution, figure 1, adsorption efficiency, figure 2, and adsorption capacity, figures 3 and 4, for the same quantity of bentonite present in the beads (8g) and the same phenol initial concentration (103.77 mg/L).

From figure 1 it can be observed that in the first 24 hours from the beginning of the experiment the highest quantity of phenol is removed. The highest drop in the concentration was observed for B5 sample, to 44 mg phenol/L from the initial 103.77 mg/L. The adsorption equilibrium was reached in 48 hours for all bentonite samples.

Figure 2 presents the evolution in time of adsorption efficiencies for all bentonite samples. Adsorption efficiency increases progressively until equilibrium is reached. Maximum values for adsorption efficiency are increasing from 12.12% obtained in case of B1 sample to 66.67% obtained in case of B5 sample. The adsorption efficiency decreases in order B5 > B2 ≅ B3 ≥ B4 > B1.

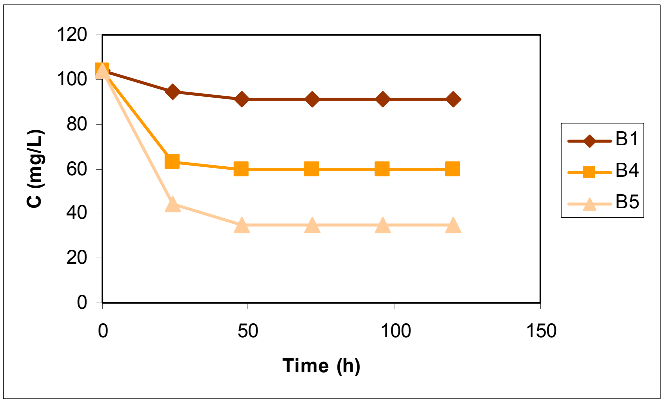

Figure 1. Time evolution of phenol concentration for three of the considered bentonites (8g bentonite, C_i = 103.77 mg phenol/L).

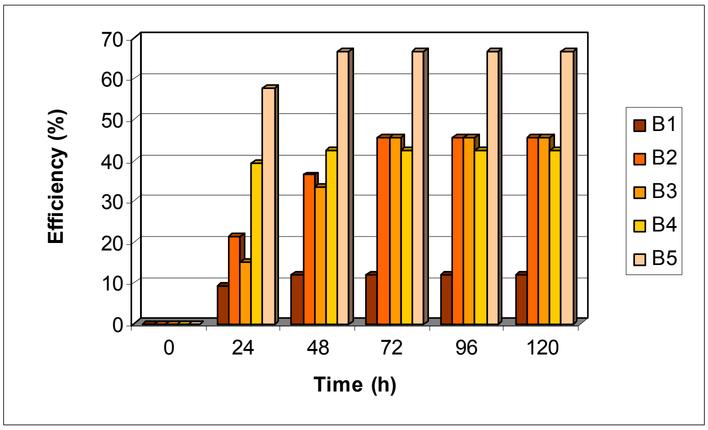

Figure 2. Influence of the bentonite type over the time evolution of adsorption efficiency for all considered bentonites (8g bentonite, C_i = 103.77 mg phenol/L).

Evolution of the adsorption process was also followed in terms of adsorption capacity, figure 3. Evolution of phenol adsorption capacity in time (not shown), follows a trend inverse proportional with concentration evolution. Therefore the adsorption capacity increases in time until equilibrium is reached, with a maximum increase after first 24 hours. Equilibrium adsorption capacities are presented in figure 3. Values between 0.1572 to 0.8648 mg phenol/g bentonite were calculated for B1 and B5 samples, respectively. The adsorption capacity decreases in the same order B5 > B2 ≅ B3 ≥ B4 > B1.

B5 bentonite sample, activated bentonite with an elevated montmorillonite content (up to 90%) and high specific surface area (around 750 m^2/g), was the most efficient sample by comparison with fibrous, powder and protein containing bentonite [15]. The activation procedure was not specified by the producer.

Taking into account the fact that B5 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.

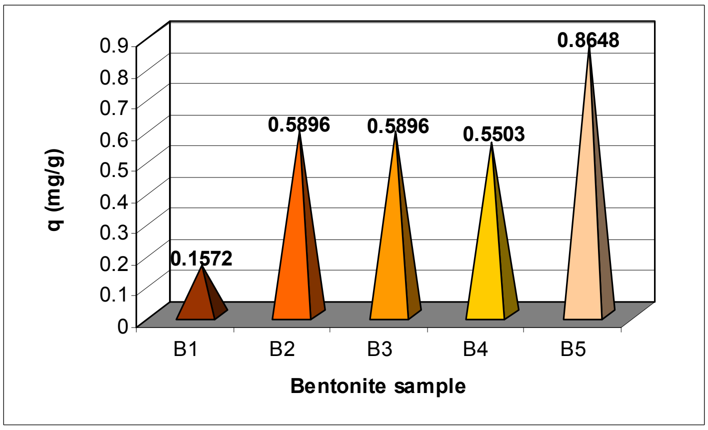

Figure 3. Adsorption capacity values for phenol removal in batch conditions (immobile phases) for all considered bentonites (8g bentonite, C_i = 103.77 mg phenol/L).

For B5 bentonite sample were also performed experiments in batch conditions under magnetic stirring (mobile phases) using the same conditions (8g and 103.77 mg phenol/L). The adsorption capacity determined in this case was calculated to be the same, but in this case equilibrium was reached in 90 minutes by comparison with 48 hours for the previous experiment. All the experiments realised from now on are realised using a batch reactor and magnetic stirring.

Bentonite quantity

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 quantities of B5 bentonite immobilized in calcium alginate beads (2-10g) at different initial concentrations of phenol in solution (31-160 mg/L). In figures 5 and 6 are presented the results obtained for C_i = 31.45 mg phenol/L and all considered bentonite quantities – 2, 4, 8 and 10g.

To have a more complete image of the adsorption process on the chosen bentonite sample, adsorption capacities were calculated in order to include in the numerical results also the bentonite quantities we used, figure 4. From the values in figure 4, 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 lead to an increase of the operating cost.

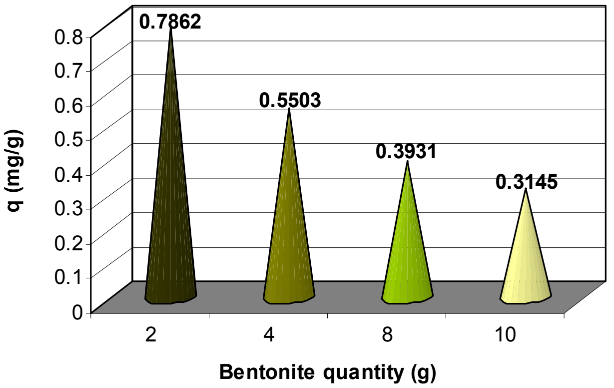

Figure 4. Adsorption capacity values for phenol removal in batch conditions (mobile phases) for different bentonite quantities (825 rpm, B5 bentonite, C_i = 31.45 mg phenol/L).

Phenol concentration in aqueous solution

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 8g of B5 bentonite immobilized in calcium alginate beads.

Influence of phenol initial concentration over the evolution of phenol concentration in time is presented in figure 5. 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 B5, increases with an increase of the phenol initial concentration, from 0.5503 to 2.2013 mg phenol/L, figure 6. Equilibrium was reached after maximum 120 minutes for all five studied concentrations.

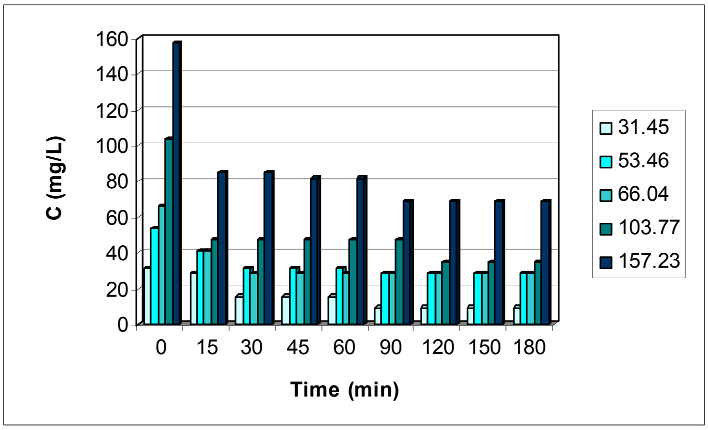

Figure 5. Influence of phenol initial concentration over the time evolution of the concentration (825 rpm, B5 bentonite, 8g).

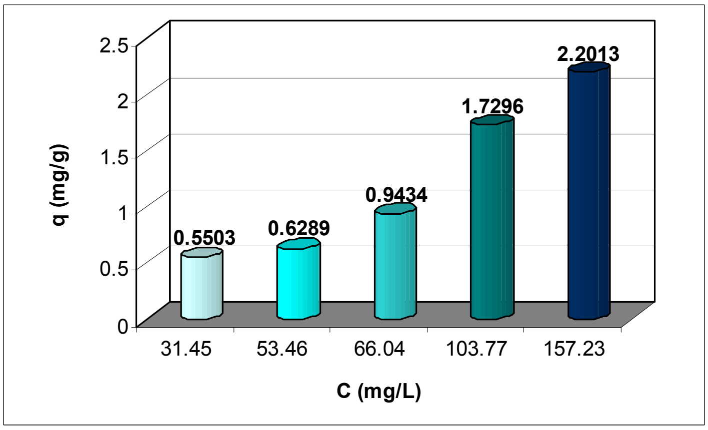

Figure 6. Adsorption capacity values for phenol removal in batch conditions (mobile phases) for different initial concentrations of phenol (825 rpm, B5 bentonite, 8g).

CONCLUSIONS

This work presents experimental results obtained in the process of phenol removal from model solutions using batch technique (magnetic stirring, 100 ml solution).

As adsorbent we used five commercial bentonites immobilized in calcium alginate beads. Influences of bentonite provenience and quantity (2-10 grams), and phenol concentration (31-160 mg/L) over the process efficiency were studied.

The adsorption capacity decreases in order B5 (Fort Benton) > B2 ≅ B3 ≥ B4 > B1 (BW200). Also, adsorption capacity increased with a decrease in the bentonite quantity and an increase of the initial phenol concentration. Maximum adsorption capacity was calculated to be 2.2013 mg phenol/g.

EXPERIMENTAL SECTION

We used five commercial sodium bentonites: BW 200 – powder sodium bentonite (B1), Gelbenton – purified fibrous bentonite (B2), Evergel – bentonite containing caseine, gelatine and egg albumine (B3), Nucleobent – powder sodium bentonite (B4) and Fort Benton Wyoming – activated bentonite (B5) purchased from Interker-wein Kft. (Hungary). The bentonite samples were used as powder, (d < 0.2 mm), without any chemical treatment. All chemicals used in this study were analytical reagent grade (phenol, alginic acid sodium salt, ethanol and $CaCl_2$).

In order to obtain the bentonite immobilized in alginate beads we used the cross-linking procedure with calcium alginate [16-19]. Thus, various quantities of bentonite (2, 4, 6, 8, 10 g) were suspended in 50-200 ml distilled water (water quantity increases with the bentonite quantity). This suspension was next blended with a mixture formed from 1 g Na-alginate and 2 ml ethanol. The mixture was then dropped with a peristaltic pump into a 0.2 M $CaCl_2$ solution. During this process, alginate-bentonite drops were gelled into beads with a diameter of 4.0 ± 0.2 mm. The Ca-alginate immobilized adsorbent beads were stored in 0.2 M $CaCl_2$ solution at 4°C for 1 hour to cure and to form the cross-linking bonds. The beads were rinsed with distilled water for remove excess of calcium ions and stored at 4°C prior to use.

For phenol adsorption study we used model 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 a batch reactor with immobile and mobile phases (phenol aqueous solution – immobilized bentonite) using 100 ml phenol solution of different concentrations, in which Ca-alginate bentonite beads obtained from the desired quantity of adsorbent were suspended. For the batch experiments realized with mobile phases, we used a magnetic stirrer operated at 825 rpm.

In order to determine the exact concentration of phenol and establish the evolution of the removal process, in batch conditions, samples of 0.5 mL (dilution in each case was 50) from the supernatant 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, until equilibrium was reached.

We studied the influence of the bentonite type and quantity, and phenol concentration in solution over the process efficiency in batch conditions. The experiments were carried out at room temperature (20°C) and without any modification of the pH value of the phenol aqueous solution.

The amount of phenol adsorbed under different conditions was calculated as adsorption capacities Q, (mg/g), while the effectiveness of the adsorption process was expressed as adsorption efficiencies E,(%); the calculated values of adsorption efficiencies and adsorption capacities should be regarded according to the precision of the determination methods we used [20].

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