ADSORPTION STUDY OF CARBENDAZIM PESTICIDE BY BENTONITE CLAY

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Abstract
Bentonite clay (BC) was used for the adsorption of carbendazim pesticide from aqueous solution. Adsorption with BC was investigated because of its large surface area and high cation exchange capacity. Influence of pH, dose of adsorbent, contact time and initial concentration of carbendazim were studied in adsorption processes by BC. Adsorption experiments were conducted in a batch system and found to be with maximum effectiveness at pH 3. The maximum recoveries of adsorption processes were 0.44mg/g and 0.25mg/g with 0.5 g and 1.0 g of BC, respectively. Contact time was 10 min and initial concentration of carbendazim was 5 mg/L for both experiments.

Introduction
The use of clay minerals as solid components in sorption of pesticide formulations is based on their adsorption properties or on formation of particular types of aggregates. The clay mineral often has to be modified by ion exchange with organic cations when used as absorbent for a pesticide [1]. However, certain bentonite can be directly used in slow-release pesticides formulations. Adsorption is used especially in the water treatment field and the investigation has to be made to determine inexpensive and good adsorbent. Clay minerals such as kaolin, bentonite are the most wide-spread minerals of the earth crust which are known to be good adsorbents/sorbents of various metal ions, inorganic anions and organic ligands [2]. BC is widely used in pesticide formulations as adsorbents or particulate fillers.
Acidic pesticides, which are often in their anionic form at the pH of soil and water environments, display a particularly high risk of ground and surface water contamination, because they are weakly retained by the most of soil types and sediment components [3]. For this reason, the development of pesticide adsorbents to prevent and remediate environmental contamination by anionic pesticides has become an important research goal [4]. Carbendazim is in a priority list for preventing the contamination of ground and drinking waters by pesticides in Europe, which considers pesticides used in quantities over 50 tons per annum and their capacities as portable or transient leachable substances [5].
The aim of this paper was to investigate the adsorption processes of carbendazim pesticide by BC. Adsorption experiments were conducted in a batch system and influence of pH, mass of adsorbent, contact time and initial concentration of carbendazim were studied.

Experimental
All chemicals used were of analytical grade. The Stock solution of carbendazim (200 mg/l) was prepared by dissolving 5 mg of standard in 25 mL of methanol. The experimental solutions of desired concentration were prepared by diluting the stock solution with distilled water. The residual concentration of carbendazim was determined by HPLC. pH of solutions were adjusted using 0.1M HCl and 1M NH_4OH.
The clay material used in the present study was commercial bentonite obtained from Republic of Serbia. The sample was washed with boiling distilled water and dried in oven at 80 °C for

12 h and crushed. BC was then sieved in order to get fractions < 160 µm. Then, it was kept in hermetically closed bottle for further uses.

Carbendazim adsorptions were evaluated at room temperature 25∘C ± 2∘C (298 K) in a 150 mL Erlenmeyer flask. Equilibrium experiments were carried out by contacting different mass (0.50, 0.75, 1.00, 1.50 and 2.00 g) of BC with 50mL of 5 mg/L carbendazim solution. The flasks were shaken on a shaker under 140 rpm and the pH value of the reaction solution was maintained at 3.0, and contact time was 30 min. to know the optimal mass. Then, at pH value 7.95 (without modification), and different pH values (3.0, 5.0, 7.0, 9.0) the experiments were initiated with the addition of 0.50 g and 1.00 g of BC.

In the following experiments, the influences of solution at pH value 3.0 were evaluated. Samples were withdrawn from the flask at pre-determined time intervals (10, 20, 30, 40, 60, 80 min) and immediately filtered by membrane filters prior to further analysis. The uptake per mg of adsorbent, qe was calculated using Eqs. (1) as follows:

$$q = \frac{(C_s - C_f)}{C_o} * V \qquad 1$$

Where q_e is the adsorption capacity (mg/g), C_0 and C_f are the initial and final carbendazim concentrations, respectively (expressed in mg/L), V is the solution volume (mL) and m is the adsorbent dosage (g).

Adsorption at different concentrations (2,4,5,6,8 and 10 mg/L) of carbendazim assays were carried out in 50-mL flask containing 50 mL of reaction solutions and 0.50 g and 1.00 g of adsorbents. The flasks were shaken on the shaker at 140 rpm.

The target pesticide carbendazim was analyzed by HPLC-DAD. Separation was performed with a reversed phase column Eclipse XDB-C18 (3 x 150, particle size 3.5µm). The operating conditions were: flow of 0.4 mlmin-1, the temperature of the column was 30ºC and injection volume of 10µL. The mobile phase consisted of water (A) and acetonitrile (B). The binary gradient elution started at 25% B in 1 minute, then linearly increased to 50% B in 5 minutes, and at the end, initial conditions were applied, 25% B for 7 minutes. The maximum wavelength of 215 nm was used.

Results and discussion
Influence of adsorption dosage
Figure 1. Shows that, a number of adsorbents (0.50, 0.75, 1.00, 1.50 and 2.00 g) at equilibrium decreased from 0.47 mg/g to 0.12 mg/g with an increase in the adsorbent dosage. The statistical analysis showed that there is a significant difference ($P \leq 0.05$) between selected clay mass at pH 3.0 and contact time of 30 min. This can be due to the competitive adsorption between the free adsorption sites and the saturated adsorption sites. Moreover, although the number of adsorption sites per unit mass of adsorbent should remain constant independently of the total adsorbent mass, increasing the adsorbent capacity in a fixed volume reduces the number of available sites as the effective surface area is likely to decrease [6].
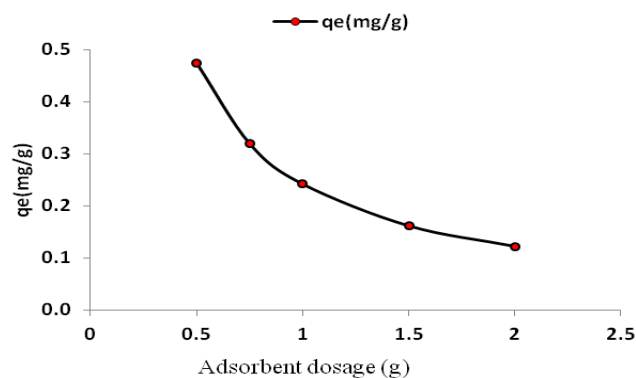
Figure 1. Effect of adsorbent dosage on adsorption of carbendazim (pH= 3, C_0= 5 mg/l, cont.time=30 min)

Influence of pH on carbendazim removal
One of the most important factors affecting the capacity of an adsorbent in aqueous solution treatment is pH. The effect of pH on carbendazim removal by BC is shown in Figure 2. The adsorption of carbendazim amount on BC increased from 0.19 mg/g to 0.44 mg/g with decrease in pH from 9.0 to 3.0 at 0.50 g of BC, and the adsorption of carbendazim amount on BC increased from 0.17 mg/g to 0.24 mg/g with decrease in pH from 9.0 to 3.0 at 1.00 g. Maximum carbendazim removal was observed at pH value 3.0. The lowest adsorbed amount was obtained at the highest pH value 9.0. The explanation of these results was that the pH value affects the ionization status of carbendazim. For instance, it can be suggested that the pH 3.0 was optimum.
Fractions of carbendazim molecules became positively charged molecules and consequently large adsorbed amount was obtained. At high pH value 9.0, a large fraction of carbendazim molecules became negatively charged or non-charged molecules. In this case BC particles cannot absorb a negatively charged carbendazim molecule due to repulsion between the negatively charged BC surfaces and carbendazim. Furthermore, the hydrophilic BC surfaces cannot adsorb large fraction from carbendazim molecules due to the hydrophobocity of carbendazim at high pH value.
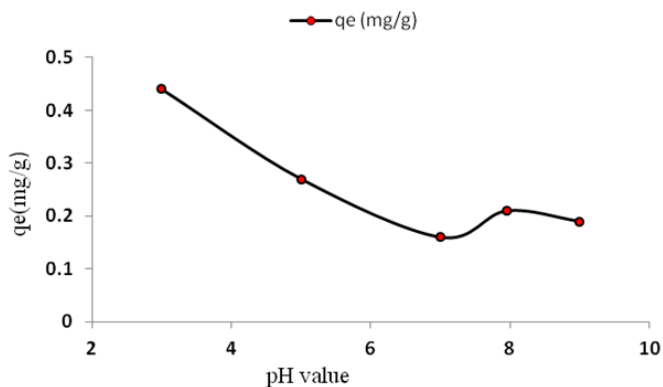

Figure 2. Effect of pH on adsorption of carbendazim by BC (C_0=5 mg/l, dosage= 0,5 g and cont.time= 10 min)

205

Influence of contact time

Adsorption of carbendazim on BC at various contact times in the solution with an initial carbendazim concentration of 5 mg/L is shown in the Figure 3. It can be clearly observed that the adsorption capacity was rapidly at the beginning of the adsorption time. The adsorption of carbendazim amount on BC reached 0.47 mg/g and 0.24 mg/g, respectively at doses 0.50 g and 1.00 g of BC when the pH value was 3.0. Prolonging the contact time could not improve carbendazim adsorption capacity significantly. There is no significant difference ($P \leq 0.05$) found between 5 min, 30 min and 40 min, and between 10 min and 20 min, and between 20 min, 30 min and 40 min. 60 min and 80 min showed the lowest q_e value at 0.50 g , pH = 3.

According to our statistical results 10 min showed the best removal of carbendazim from aqueous media when the pH value was 3.0 and the mass of BC was 0.5 g and 1.0 g.

Figure 3. also depicts the evolution of the amount of carbendazim uptake with the contact time. The adsorption capacity of carbendazim increased with time and reached equilibrium after 10 min. The adsorption is quiet fast and attained a maximum after 5 min of contact, then followed a gradual decrease with time until it reached equilibrium. This may be due to the fact that, at the beginning, the surface adsorption sites were readily available and consequently, adsorption proceeded at very high rate, then, with increasing coverage, the number of sites became less and carbendazim ions had to fiercely compete among themselves for getting.
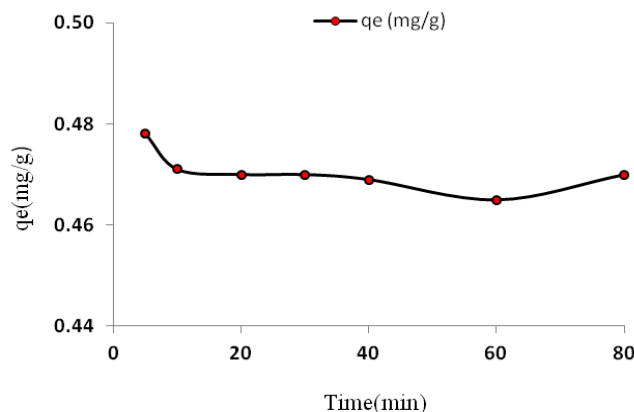

Figure 3. Effect of contact time on adsorption of carbendazim by BC (c_0= 5 mg/l, dosage=0,5 g, pH 3)

Influence of initial concentration

Figure 4. show the adsorption uptake versus initial concentration for an equilibrium time at 10 min. The amount of carbendazim removed at equilibrium decreased from 0.50 mg/g to 0.21 mg/g at 0.50 g of BC with the increase in concentration from 2 mg/L to 10 mg/L. There is no significant difference ($P \leq 0.05$) between concentrations 2.0 (mg/L) and 4.0 (mg/L) .and between 5.0 (mg/L) and 6.0(mg/L). 10 (mg/L) possessed the lowest qe value when the pH value was 3.0 and the mass of BC was 0.50 g.

The highest qe value ($P \leq 0.05$) was registered at 2 (mg/l) when the mass of BC was 1.00 g and the pH value was 3.0 and contact time 10 min.
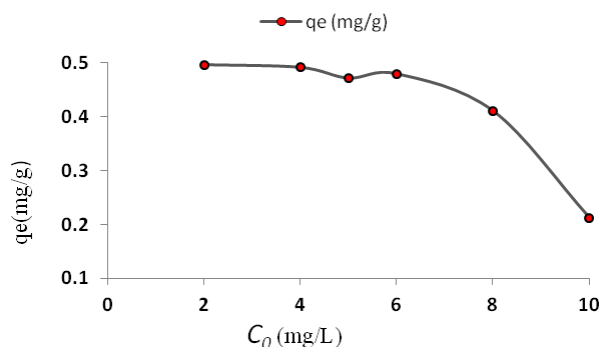
Figure 4. Effect of initial concentration on adsorption of carbendazim by BC (cont.time=10 min, dosage=0,5 g, pH 3)

The amount of carbendazim removed was 0.25 mg/g at equilibrium for 1.0 g of BC and was no significant difference in concentration from 2 mg/L to 10 mg/L. It is clear that the adsorption capacity depends on the initial concentration and amount of BC. This is due to the fact that, the initial carbendazim concentration provided the necessary driving force to overcome the resistances to the mass transfer of carbendazim ions between the solution and adsorbent [7].

Conclusion

The study shows that BC, natural material, can be used as an adsorbent for removal of carbendazim from aqueous solutions. The adsorption characteristics of carbendazim in aqueous solution were shown to be influenced by several factors. The adsorption was highly dependent on the dosage of BC, pH and concentration of carbendazim. The result of the present investigations showed that BC has higher adsorption efficiency. The adsorbed amount of carbendazim increased as initial carbendazim concentration decrease.

In our study, carbendazim adsorption from aqueous solution was carried out by bentonite clay (BC). The mechanisms of carbendazim adsorption onto BC could be attributed to ion-exchange, surface complexion, and surface precipitation. The economic evaluation implied that adsorption process was cost-effective.

Acknowledgement

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