

Development of controlled release formulations of thiabendazole

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ABSTRACT

This study aimed to develop controlled release formulation of Thiabendazole for reduced contaminations to soil water and agricultural produces. The idea behind this work was based on changing the ionization status of Thiabendazole molecule throughout pH changes to become a cation then adsorbing it to bentonite clay surfaces. Equilibrium concentrations of Thiabendazole in the adsorption solutions were determined by HPLC. Results showed that Thiabendazole was better adsorbed in clay at the lowest pH value (pH 3). Furthermore, raising the temperature of the adsorption reaction increased the adsorbed amount of Thiabendazole. Release experiments showed that Thiabendazole is extremely slower at pH 3 than at pH 5.5 or pH 9. These promising results suggest that application of Thiabendazole clay based formulation may reduce the applied rate and that the released fraction consequently may reduce the environmental contamination. It is also advantageous to use these formulations in the acidic soil for plant disease control.

KEYWORDS

Thiabendazole; Adsorption; Controlled Release; pH; Bentonite

1. INTRODUCTION

Fungicides are essential agricultural materials needed to protect the agricultural products and to improve its quality. However, the frequent applications of fungicides to control plant diseases may have resulted in accumulation of their residues in plant tissues. Previous review

[1] showed that residues of pesticides have been detected in many agricultural products in the Middle East countries. For instance fenitrothion residues were detected in potato sample from Egypt [2], dicofol residues were detected in cucumber in Jordan [3], captan, thiabendazole, vinclozolin fenuron residues were detected in many agricultural products in Kuwait [4], fenvalerate residues were detected in apple samples in Pakistan [5], atabron triadiminol residues were detected in tomato and potato samples in Palestine [6], captafol residues were detected in a wheat monoculture after prolonged application in Germany [7], fludioxonil residues were found in citrus fruits in Italy [8]. However, fungicide residues have been detected in runoff from golf courses, under Scandinavian conditions [9], tricyclazole residues were found in rice paddy watersheds in Italy [10]. Carbendazim residues were detected in surface water samples in Chile [11]. Thiabendazole residues have been detected in citrus samples [12], in fruit-based soft drinks [13], in apple juice concentrate [14], in lemons [15], in water samples [16], in sea port water and in sediment samples [17], in food-stuffs [18], in the UK mushroom industry [19]. Furthermore, Thiabendazole application creates eco-toxicity, for instance, Castillo *et al.* [20] found a macroinvertebrate community changes following thiabendazole applications in a banana plantation. Kim *et al.* [21] studied the Sorption of benzimidazole anthelmintics to dissolved organic matter and sewage sludge. They found that the correlations between $\log K_{oc}$ and $\log K_{ow}$ were weak and the magnitude of the sorption coefficients to the hydrophilic organic matters (hydroxypropyl-beta-cyclodextrin and sewage sludge) were similar to or slightly smaller than those for the hydrophobic organic matters (humic acids and liposome).

García Calzón *et al.* [22] studied the adsorption of Thiabendazole at a Mercury/Solution Interface. They found a state of normal adsorption and a condensed two-

dimensional layer at moderately charged and rather negatively charged surfaces. Spanoghe *et al.* [23] studied the fate of Thiabendazole during storage, handling and forcing of chicory. They concluded that Thiabendazole residues applied before storage are still present on the roots at the start of the forcing cycle. Furthermore, previous study [24] indicated that Thiabendazole appears to have some mobility in sand, silt loam, and sandy loam, but shows no mobility in clay. As obvious, residues of Thiabendazole have been found in many agricultural products and environmental samples. These residues may have adverse human health effects. Consequently, initiative steps must be taken to reduce the accumulation of these residues in fruit, vegetable and environmental samples and consequently reduce the health hazards. One approach to achieve this is to adsorb Thiabendazole molecules to clay minerals under different pH values that change the ionization status of Thiabendazole from hydrophobic and/or anionic form to cationic one consequently it can strongly be adsorbed to clay surface via cation exchange reaction.

This study is initiated to develop clay based formulations that controlled the release of Thiabendazole to soil environment consequently reduce the possible accumulation in plant tissues and to investigate the effect of different parameters on the fate of Thiabendazole.

2. MATERIALS AND METHODS

Materials. We used a Ca^{2+} -bentonite from Greece (Milos, Prassa Carys, mined 1992, M48). The reason behind using a Ca^{2+} -bentonite clay because it contains about 95% Ca^{2+} -montmorillonite which have high cation exchange capacity (CEC) ranged 80 - 120 mmol/g clay [25]. Thiabendazole (HPLC grade, 2-(thiazole-4-yl)benzimidazole; 2-(1,3-thiazol-4-yl) benzimidazole, molecular weight 201.3, (Figure 1) was purchased from Fluka (Germany). It is hydrophobic with an octanol/water partitioning coefficient $K_{ow} \log P = 2.39$ (pH 7), and solubility in water 160 mg/L (pH 4), and 30 mg/L (pH 7 - 10). It has a pKa value 4.73 [26].

2.1. Adsorption Experiments

Influence of time on the adsorption of Thiabendazole: The stock solution of Thiabendazole was prepared by dissolving 31.9 mg in 2 - 3 mL methanol and diluting to 1 L with deionized water. The low concentration of methanol in the adsorption experiments had no influence on linuron adsorption.

Appropriate amounts of Thiabendazole equivalent to 30 mg/g clay were transferred to a 30 ml centrifugation tubes and diluted with water up to 25 ml. The tubes were kept under rotary shaking for 4, 6, 24 and 30 hr. The tubes were centrifuged at 20,000 g to separate the clay par-

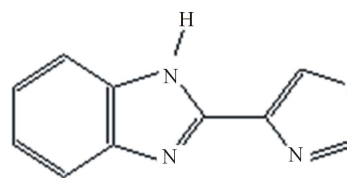


Figure 1. Chemical structure of Thiabendazole.

ticles. The equilibrium concentrations of Thiabendazole in supernatants were determined by HPLC as described below.

2.2. Adsorption Isotherm

The adsorption of Thiabendazole on the bentonite was measured at $22^\circ\text{C} \pm 2^\circ\text{C}$. Appropriate aliquots of the aqueous stock solution of Thiabendazole were diluted with water to 25 mL and added to 5 mg bentonite in 30-mL centrifuge tubes. The concentration of Thiabendazole ranged between 1.2 and 31.9 mg/L. The final concentration of bentonite was 0.2 g/L. The dispersions were kept under continuous rotary agitation during 48 hours. The supernatant was separated by centrifugation at 20,000 g for 0.5 h.

The concentration of Thiabendazole in the supernatants was determined by Waters 717 HPLC with UV detector (detection wavelength 299 nm). Column: Nova-Pak C18 (inner diameter 3.9 mm, length 150 mm), flow rate: 1 mL/min. The mobile phase was methanol/water 50/50 (v/v). The water phase contained 0.5% ammonium hydroxide (25%). The run time was 6 min and retention time is $\sim 3.825 \pm 0.124$. The injection rate was 25 μl .

The relationship between concentrations of Thiabendazole and peak areas of the HPLC chromatogram was linear for 0.388 - 6.38 mg/L Thiabendazole. Linear regression was used to determine the equilibrium concentration of Thiabendazole in the solutions. The regression showed R^2 value close to unity (0.9997). The amount of Thiabendazole adsorbed (correctly the specific reduced surface excess $n^{\sigma(n)}/m$) was calculated from the depletion of the Thiabendazole concentration by adsorption [27].

For each isotherm a reference solution with an intermediate concentration was stirred without bentonite to evaluate adsorption on the glass or other losses. Analysis showed that Thiabendazole was not adsorbed on the glass of the centrifuge tubes. All adsorption experiments were made in duplicate.

2.3. Influence of pH Values on the Adsorption of Thiabendazole

Adsorption of Thiabendazole on bentonite was measured at various pH values (3, 5.5 and 9). In this procedure appropriate aliquots of an aqueous solution of

Thiabendazole (31 mg/l) was dissolved in 1 L distilled water as mentioned above. Solutions of pH 3 and pH 5.5 were obtained by addition of few drops of acetic acid to distilled water in two separate jars whereas solution of pH 9 was obtained by addition of few drops of ammonium hydroxide to distilled water in a separate jar. These solutions were used for adsorption and release experiments.

In the adsorption experiments, appropriate amounts of Thiabendazole were diluted in 25 ml with distilled water having the pH values mentioned above. The concentrations range of Thiabendazole in all adsorption experiments under the mentioned pH values were 0.0 - 31.9 mg/L. Each adsorption tube in all experiments contained 5 mg bentonite. The adsorption solutions were maintained at pH 3, 5.5 and 9. The final concentration of the clay was 0.2 g/L. The supernatants were separated by centrifugation at 20,000 g for 1 h, and Thiabendazole in the equilibrium solutions were determined by HPLC.

2.4. Influence of Temperature on the Adsorption of Thiabendazole

To measure the effect of temperature on the adsorption of Thiabendazole, the adsorption experiments mentioned above were maintained at 278, 291 and 313 K at pH 3. The remaining concentrations of Thiabendazole were determined by HPLC as mentioned below, in each tube was determined by HPLC as described above.

2.5. Preparation of Clay Based Thiabendazole Formulations

Appropriate amounts of Thiabendazole (31 mg) were dissolved in 1 liter of distilled water to form a stock solution. Appropriate amounts of Thiabendazole 13 mg/g clay complex was added to a 1 L volumetric flask containing 1 g of clay and various pH solution (3 - 9). The samples were kept for 48 h under continuous magnetic stirring. The clay-Thiabendazole complexes were separated by centrifugation at 6000 g, air dried and kept in plastic bottles at room temperature for use. The adsorbed amounts of Thiabendazole on the clay were determined by HPLC as mentioned above.

2.6. Release of Thiabendazole from Clay Based Formulation

Release of Thiabendazole from different formulations was conducted using Buchner funnel. In this procedure, 50 g of air dried sandy soil was mixed through a glass cylinder with 20 mg bentonite-Thiabendazole formulation containing 1 mg Thiabendazole (Figure 1). The soil mixture was transferred to a Buchner funnel (10 cm internal diameter) has a filter paper in the bottom. The soil layer was homogenized to a 0.5 - 1 cm height. The

soil layer in each funnel was carefully irrigated with 500 ml water having different pH values as mentioned above. Each volume of water (500 ml) was applied in ten portions during 2.5 hours. Each washing (50 ml) was collected after 30 min of application in a separate flask and analyzed by HPLC to determine the released fraction of Thiabendazole. The experiment was conducted with two replications to each pH value.

2.7. Data Analysis

Adsorption data were collected as an average of 3 replicate and the standard deviation was calculated and used as error bars to discriminate differences among isotherms. Presenting the standard deviation as an error bar is the best method to determine significant differences among adsorption isotherms. Variances among treatments were analyzed by calculating p-values associated with the t-test. Values < 0.05 indicated significant difference. It is well known that overlapping error bars indicate no difference, whereas small or extremely small error bars indicate a significant difference. Adsorption data of each isotherm were fitted by the Freundlich equation to calculate the adsorption parameters (K, and n).

3. RESULTS AND DISCUSSION

3.1. Adsorption Kinetics

The adsorbed amounts of Thiabendazole (Figure 1) by raw bentonite at different agitation time are shown in Figure 2. It can be seen that the adsorbed amounts are 18.33 ± 0.63 , 17.82 ± 1.17 , 19.09 ± 0.43 , and 19.94 ± 0.2 mg/g, after 4 hr, 6 hr, 24 hr and 30 hr respectively. However, the average adsorbed amount of all cases is 18.8 ± 0.92 mg/g. Statistical analysis showed no significant differences among the adsorbed amount at different time.

Furthermore, it is obvious that the standard deviation is very low indicating homogeneous values of average adsorbed amounts. Accordingly, it can be suggested that 4 hr to 6 hr is enough agitation time for the adsorption experiments. Similar results were previously obtained for other cases [28].

3.2. Influence of pH on Thiabendazole Adsorption

Adsorption of Thiabendazole on raw bentonite at different pH values is shown in Figure 3. It can be seen that the highest adsorbed amount of Thiabendazole was obtained at the lowest pH value (pH 3) and the adsorbed amount decreased as the pH value increased. The lowest adsorbed amount was obtained at the highest pH value (pH 9). The explanation of these results is that pH value affects the ionization status of Thiabendazole. For

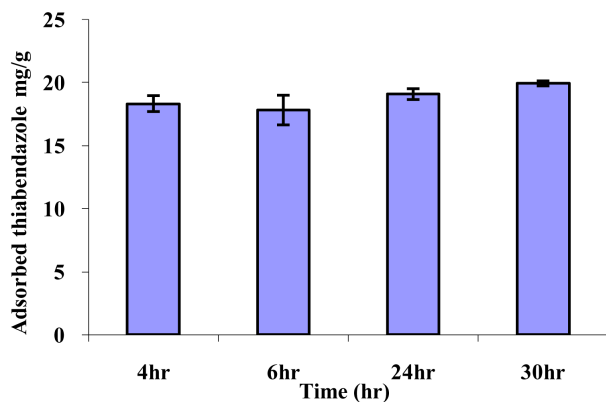


Figure 2. Adsorption kinetics of Thiabendazole on M48 at 40°C. Bars represent standard deviation.

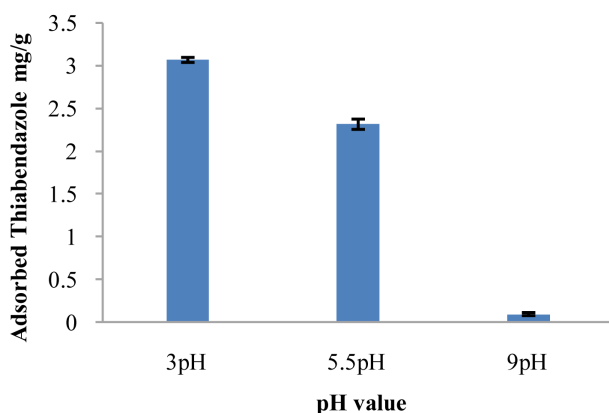


Figure 3. Adsorption of thiabendazole on M48 at different pH values. Bars represent standard deviation.

instance, it can be suggested that at pH 3 or pH 5.5 large fractions of Thiabendazole molecules became positively charged molecules consequently large adsorbed amount were obtained. At high pH value (pH 9) large fraction of Thiabendazole molecules became negatively charged or non charged molecules. In this case raw bentonite particles can not adsorb a negatively charged Thiabendazole molecule due to repulsion between the negatively charged bentonite surfaces and Thiabendazole. Furthermore, the hydrophilic bentonite surfaces can not adsorb large fraction from Thiabendazole molecules due to the hydrophobicity of Thiabendazole at high pH value. The effects of pH values on the ionization status of Thiabendazole molecules are shown in **Figure 4**. Our suggestion is supported by the previous results of El-Nahhal and Safi [29], who provided acceptable ionization status of bromoxynil adsorption on organo-clays and by Rodriguez *et al* [30] who achieved Thiabendazole separation using a buffer of formic acid-ammonium formate at pH 3.5 with 2% of methanol using solid phase extraction.

In addition, further support to our discussion can also be obtained from previous reports [24,31] who provided

different K_{ow} logP values for Thiabendazole at different pH values.

3.3. Adsorption Isotherms at Different pH

Figure 5 illustrates the adsorption isotherms of Thiabendazole on bentonite clay different pH values. As expected, Thiabendazole was poorly adsorbed on raw bentonite (M48) high pH (pH 9), whereas low pH (pH 5.5 and pH 3) significantly enhanced the adsorbed amounts of Thiabendazole. It can be seen that at low equilibrium concentration (less than 0.5 mg/l) a sharp increase in the adsorbed amounts of Thiabendazole was observed. Increasing Thiabendazole concentration in the equilibrium solution did not produce further increase in the adsorbed amount of Thiabendazole, and the adsorption reached to plateau. This feature of adsorption was obtained in the organic cation and clay minerals. Moreover, reaching a plateau suggests that the available adsorption site in bentonite surfaces were nearly occupied by Thiabendazole molecules. Similar feature was obtained with adsorption of cationic herbicides, paraquat and diquat, adsorption on clay [32] and organic cations to clays [25]. The explanation of pH effect on the adsorption of Thiabendazole is given above.

Figure 3 shows the adsorption isotherms of Thiabendazole on bentonite at various pH values.

Thiabendazole has an acid dissociation constant (pKa) of 4.73 and is mostly neutral at pH < 4.73, becoming deprotonated (anionic) at pH > 7.

Accordingly, the adsorbed amount of Thiabendazole obtained at pH 3 is higher than the adsorbed amount

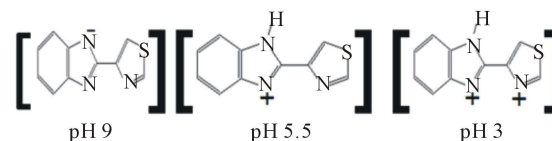


Figure 4. Influence of pH value on the ionization status of Thiabendazole.

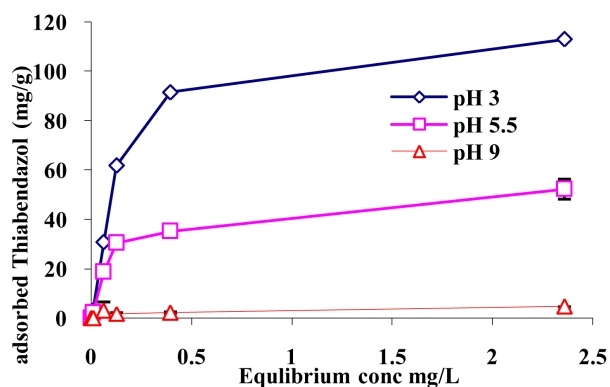


Figure 5. Adsorption of Thiabendazole on clay (M48) at various values of pH at 291 K.

obtained at pH 5.5 and pH 9 (Figure 3). Statistical analysis showed a significant difference, p-value with t-test = 0.004.

The high adsorbed amount at pH 3 was because, at pH 3, Thiabendazole molecules are mostly protonated, and have 2 positive charges in the N-atoms, in this case they may be adsorbed as cations on hydrophilic sites of the bentonite surfaces. At pH 5.5, a part of Thiabendazole molecules has a one positive charge in the N-atoms and the other part is in the neutral form (Figure 4). In this case, the one positive charged molecules are adsorbed on the hydrophilic sites of bentonite surfaces, and the neutral forms stay in solution; accordingly, low adsorbed amounts of Thiabendazole molecules were observed. At pH 9 the majority of Thiabendazole molecules are negatively charged or in equilibrium with the neutral form. In this case the negatively charged molecules stay in the solution due to the electronic repulsion between the anionic form of Thiabendazole and the negatively charged bentonite surfaces. Moreover, very little of the neutral Thiabendazole molecules are adsorbed the negatively charged bentonite surfaces through water bridge. The low adsorption in this case is due to the hydrophilic surface of bentonite particles and the hydrophobic properties of Thiabendazole molecules. This explanation is supported by previous reports of [29] that found a high adsorbed amount of bromoxynil in soil and wheat char at low pH. Furthermore, the shape of the isotherm tends to be L-type and adsorption occurs as the Langmuir type at various pH values, due to changes in the electronic form of Thiabendazole a result of pH changes.

Furthermore, the shape of the isotherms was similar in all cases. According to Gile *et al.* [33] classification, isotherms of Thiabendazole could be classified as L type based on the initial slope of the curve in the concentration range studied. Adsorption isotherms were regular, positive and concave to the concentration axis (Figures 5 and 6), which indicated no strong competition for the adsorption sites between the solvent (water) and Thiabendazole molecules on bentonite surfaces. This suggests that Thiabendazole adsorption becomes easier as its concentration in the aqueous phase rises. These isotherms indicate the tendency of large adsorbed molecules to associate rather than to remain as isolated units. Fitting the data in Figures 5 and 6 to the Freundlich equation gives the adsorption parameter, ($Q = KC^{1/n}$) where Q is the adsorbed amount in mg/g, C is the equilibrium concentration of Thiabendazole, K reflects the binding coefficient, and n is the physical adsorption parameter.

It can be seen in Table 1 that the K value of adsorption on raw bentonite at pH 3 is several times higher than at pH 5.5 and pH 9, indication the high affinity of Thiabendazole to bentonite surfaces at low pH. Furthermore, the binding coefficient (K) is the highest at 291 K. This

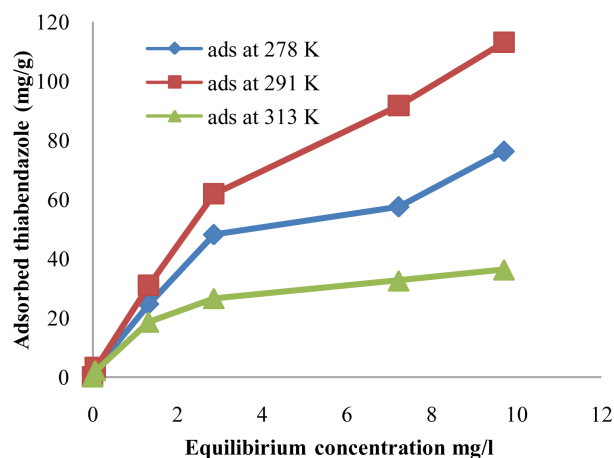


Figure 6. Influence of temperature on the adsorption of Thiabendazole on M48. Bars represent standard deviation.

Table 1. Physical parameters of Thiabendazole adsorption at different conditions.

Adsorption condition	K	n	R ²
pH 3	332	1.02	0.9392
pH 5.5	8.41	1.50	0.9865
pH 9	0.21	1.02	0.8634
278 K	18.92	1.54	0.9839
291 K	24.21	1.4	0.9936
313 K	6.94	1.55	0.9571

suggests that the optimum adsorption occurred at 291 K. Furthermore, the regression values (R²) in all cases are close to 1 indication of a strong positive association.

3.4. Adsorption Isotherms at Different Temperature

Adsorption of Thiabendazole at different temperature degrees are shown in Figure 6. It can be seen that adsorption of Thiabendazole is more pronounced at 291 K than at 278 K and at 313 K. The explanation of these results is that at a low temperature (278 K), the chemical potential of Thiabendazole molecules is reduced and the molecules tend to form crystals due to their low solubility in water, 0.16 g/l, 20°C [26]. At 291 K, nearly the optimum temperature of solubility in water, Thiabendazole molecules are very active and interact with the adsorption site at the bentonite surfaces accordingly high adsorbed amount of Thiabendazole was observed. In contrast, at high temperature (323 K), the system absorbs heat energy and an increase in the chemical potential of Thiabendazole molecules may occur. This step makes more Thiabendazole molecules in a dynamic mobility in the aqueous solution; accordingly, low adsorption was observed, indicating low adsorption affinity at high temperature. Statistical analysis of the data in Figure 6 indi-

cates significant difference among the adsorbed amount at 278, 291 and 323 K, as the error bars which represent the standard deviation do not overlap at any point of the equilibrium concentration (Figure 6). Furthermore calculation of p-values among the three isotherms showed value ranges between 0.034 - 0.029, indicating significant differences among all cases.

This supports the suggestion that optimal adsorption occurred at temperature 291 K.

Changes in molar free energy (ΔG°) of the adsorption reaction of Thiabendazole at different temperatures were calculated using the following equation [21]:

$$\Delta G^\circ = -RT \ln C_i/C_e$$

where, ΔG° is the molar free energy change (Kcal mol^{-1}), R is the gas constant ($1.986 \text{ cal K}^{-1} \text{ mol}$), T is the absolute temperature of the adsorption reaction, and C_i/C_e are the initial and equilibrium concentrations, respectively.

The values of ΔG° for adsorption at 278 K, 291 K and 313 K from distilled water were $-0.802 \pm (0.313)$, $-2.147 \pm (0.504)$ and $-0.369 \pm (0.18)$, respectively. These results are in accordance with the data in Figure 6. These values are within the expected range for physical adsorption [34]. Analysis of variance between the calculated free energy at 278 K and 291, and between 291 and 313 gave p-values of 0.0005 and $8.86\text{E}-06$ respectively.

3.5. Release of Thiabendazole

The release of Thiabendazole from bentonite-Thiabendazole complexes at different pH values are shown in Figure 7. It is evident that % released fraction of Thiabendazole at pH 3, pH 5.5 and pH 9 are: 1.48 ± 0.05 , 25.71 ± 4.46 and 79.88 ± 9.8 respectively. The explanation of these results is that adsorption of Thiabendazole at low pH values (3, 5.5) tends to be attraction between the positive charge of Thiabendazole (Figure 4) and the negative charge of the Ca-bentonite clay. This interaction is very strong, accordingly the release of Thiabendazole molecules from the clay surfaces depends on the pH of added water and the possibility of Thiabendazole molecules to form hydrogen bonding with water molecules.

Under low pH values (pH 3, 5.5), the electrostatic interactions between Thiabendazole molecules and water is stronger than the hydrogen bonding with water molecules accordingly low fraction of Thiabendazole is available for solubility and release at water has low pH value. Under high pH value (pH 9), the electronic status of Thiabendazole changed from positively charged molecules to a neutral or negatively charged ones. Accordingly the possibility of hydrogen bonding between Thiabendazole and water molecules is very high beside the fact that the electrostatic interaction between Thiabendazole and Ca-bentonite clay became very weak. Accordingly, high

fraction of Thiabendazole is available for release as evident in Figure 7.

Kinetics of Thiabendazole release at different water volumes are shown in Figure 8. It can be seen that upon application of 0.05 L water (first washing) about 80% of the initial Thiabendazole concentration was released from raw bentonite-Thiabendazole complex at pH 9, whereas 26% and 1.5% Thiabendazole concentrations were released at pH 5.5 and pH 3. Further application of eluting water up to 500 ml resulted in the further release of Thiabendazole up to 97%, 70% and 2.6% from raw bentonite-Thiabendazole at pH 9, pH 5.5 and pH 3 respectively. Thus, the release of Thiabendazole from bentonite-Thiabendazole complex at pH 3 was significantly slower than at pH 5.5 and pH 9.

The explanation of these results is that the release of Thiabendazole from bentonite-Thiabendazole complexes is controlled by the binding coefficients, (K) values, which are very high at pH 3 and pH 5.5 and low at pH 9 (Table 1). These results are in agreement with a previous report [28], which found that herbicide release was controlled by binding coefficients. These results are in accordance with the adsorption data (Figure 5).

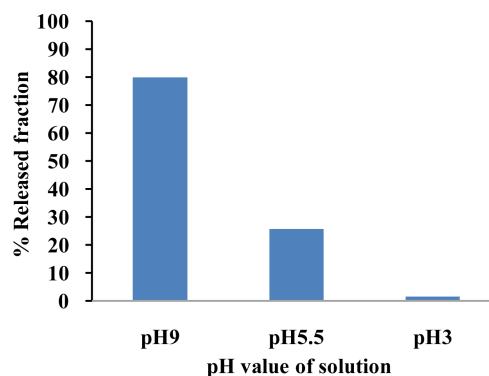


Figure 7. Influence of solution pH on the release fraction of Thiabendazole from bentonite (M48). Bars represent standard deviation.

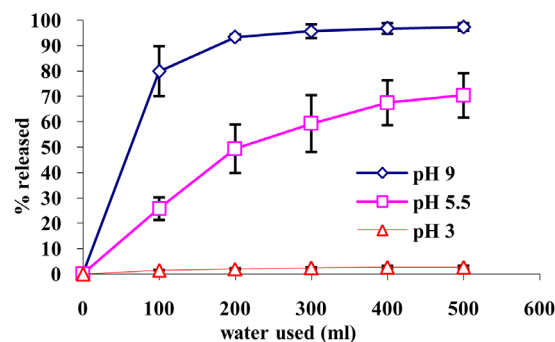


Figure 8. Kinetics of Thiabendazole release from bentonite (M48) at different solutions pH. Bars represent standard deviation.

4. CONCLUDING REMARKS

This study reveals that changing the solution pH of Thiabendazole resulted in changing the ionization status of the molecules and consequently enabled them to be adsorbed on the hydrophilic bentonite surfaces. The rationale for this work is that adsorption of Thiabendazole on bentonite surfaces can be enhanced by changing solution pH. These findings showed that the highest adsorbed amounts were obtained at pH 3 and at 291 K (Figures 3 and 6). The release of Thiabendazole was very slow from bentonite complexes at lower pH (Figures 7 and 8). The environmental relevance of this work is that bentonite clay can be used to develop environmentally acceptable Thiabendazole formulations for safe controlled release formulation.

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