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Removal of Organic Pollutant from Water by Modified Bentonite

Y. El-Nahhal and J. Safi

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1. Introduction

Bromoxynil is a nitrile herbicide, widely used in the region for annual weed control. Its application creates environmental contaminations. For instance, it was detected in air samples [1], water samples [2], and soil samples [3]. Its application may create health problems [4]. Furthermore, bromoxynil has been reported as a toxic agent to important green algae in the ecosystem [5], more over, it is recently indicated that bromoxynil was among eight-herbicide mixture, that produced negative effects on microbial communities even at low concentrations [6].

Application of commercial formulations of bromoxynil (emulsion concentrate, and/or suspension concentrate) in the ecosystem may induce species shifts within the communities and could affect the structure and the function of the aquatic communities [7].

Several methods have developed to remove organic pollutants from water. This includes adsorptive techniques [8], photochemical methods [9-11] activated carbon [12], carbon nanotubes [13], gamma-MnO₂ [14] and combined nano MgO-nanofiltration technique [15]. Worldwide, very little information about removal of bromoxynil from water are available, beside the fact that no attempt has been made in Gaza to remove or attenuate bromoxynil concentration in the ecosystem.

The objectives of this study are: 1) to design suitable organo-clay complexes and 2) to optimize the aquatic pH to enhance removal of bromoxynil from water.

2. Materials and methods

Materials. Ca²⁺-bentonite clay (M48) with cation exchange capacity (CEC) equivalent to 960 mmol(+) kg⁻¹ (= 0.96 meq g⁻¹) [16] was used. The organic salts used are: N-cetylpyridinium bromide (NCP⁺Br⁻) and N-hexadecyl tributylphosphonium bromide (HDTBP⁺Br⁻). The

organic pollutant used is Bromoxynil (HPLC grade, 3,5-dibromo-4-hydroxybenzotrile). Those materials were purchased from Sigma Chemical Co., Germany.

Synthesis of organo-Bentonite complexes. The organo-Bentonite complexes were synthesized by simple ion-exchange reaction. In this procedure, 5 mmol of the solid organic salt was added to 1L of 1% (w/v) aqueous suspension of Bentonite clay (M48) under stirring conditions for 3 days [16].

Bromoxynil stock solution was prepared by dissolving 31 mg in 2-3 mL methanol and diluting to 1 L with deionized water.

2.1. Removal of bromoxynil from water

In this experiment 0.5 mg of bromoxynil was added to various glass centrifuge tubes containing 10 mg of different organo-Bentonite. The tubes were shaken for 48h and then the supernatants were collected by centrifugation at 20000g. The remaining concentration of bromoxynil in the supernatants were determined by HPLC.

2.2. Influence of bromoxynil concentrations on the removal process

Thirty ml of bromoxynil concentrations ranged between 0.66-31 mg/L were transferred to 30-mL glass centrifuge tubes containing 0.005 g organo-Bentonite. The tubes were kept under continuous rotary agitation for 48 hours to maintain aqueous suspension during the experimental time. This experiment was maintained at pH7. Control samples were made by performing the same procedures under the same conditions without adding the organo-Bentonite to each tube. The aqueous solutions were collected by centrifugation at 20,000 g for 0.5 h.

2.3. Influence of pH on removal of bromoxynil

Deionized water was used to perform the removal experiments at pH 7, whereas few drops of acetic acid were added to the stock solution of bromoxynil to adopt the pH to 3.

The removal experiments were performed as described above using HDTBP-Bentonite complex.

2.4. Influence of Temperature on removal of bromoxynil

To measure the effect of temperatures on the removing process of bromoxynil, the experiments described above were performed at 5, 17 and 40 ± 2 °C using NCP-Bentonite complex as a removing materials

2.5. Release of bromoxynil from organo-bentonite complexes

To insure removal of bromoxynil from water, the used organo-bentonites in the above mentioned experiments were collected, air dried and used for bromoxynil extraction. In this experiments the air dried organo-bentonites were transferred to test tube containing 5 ml of

water methanol mixture as described in mobile phase (section 2.8). The test tubes were transferred to an ultrasonic machine functioning at high speed for 3 min. the solution was collected and additional 5 ml of water methanol mixture was added again and the same procedure was repeated to insure maximum extraction. Concentration of bromoxynil in the solution was determined as mentioned above.

2.6. Measurements of bromoxynil

The concentrations of bromoxynil in the supernatants were determined by Waters 717 HPLC with UV detector (detection wavelength 283 nm). Column: Nova-Pak C18 (inner diameter 3.9 mm, length 150 mm), flow rate: 1 mL min⁻¹. The mobile phase was methanol/water 50/50 (v/v). The amount of bromoxynil adsorbed was calculated from the depletion of the bromoxynil concentration in the aqueous solutions.

2.7. Data analysis

The removal data were collected as an average of 3 replicate and the standard deviation was calculated and used as error bars to discriminate differences among treatments. Presenting the standard deviation as error bar is the best method to determine significant differences among adsorption isotherms. It is well known that overlapping of error bars indicating no difference whereas small or extremely small error bars indicate significant difference.

3. Results and discussion

The cationic quaternary ammonium/phosphonium salts used in this study are solid materials at room temperature, and surface-active agents (surfactant), The molecular structures include an aliphatic part and/or an aromatic ring. In a diluted solution (< 0.1 mmol/g) the adsorbed amounts of surfactant on bentonite surfaces were nearly similar (Data not shown), whereas as high added concentration (>0.5 mmol/g) the extent of adsorption became a function with the size and shape of the surfactant. Large organic cations can effectively displace inorganic cation such as Ca²⁺ and/or Na⁺ from mineral surfaces of clay by ion exchange [17]. More detailed results are presented in El-Nahhal and Lagaly [16].

Removal of bromoxynil from water by different organo-bentonite complexes are shown in Figure 1. It can be seen that the removed amounts of bromoxynil on raw Bentonite (clay) or modified Bentonite with NCP and/or HDTBP, are: (14.6±3.65); (84.65± 8.12) and (46.48± 27.25) mg/g respectively.

The largest removed amount of bromoxynil was observed on bentonite modified with NCP followed by HDTBP. The explanation of these results is that low removed amount using raw Bentonite is due to the hydrophilic surfaces of Bentonite and hydrophobic nature of bromoxynil. Modification of Bentonite surfaces with NCP or HDTBP may have created a microscopic organic phase on Bentonite surfaces as in hexadecyltrimethyl ammonium-smectite [18]. This situation may acts as a solubilizing (partitioning) medium for removing nonionic organic compounds from water

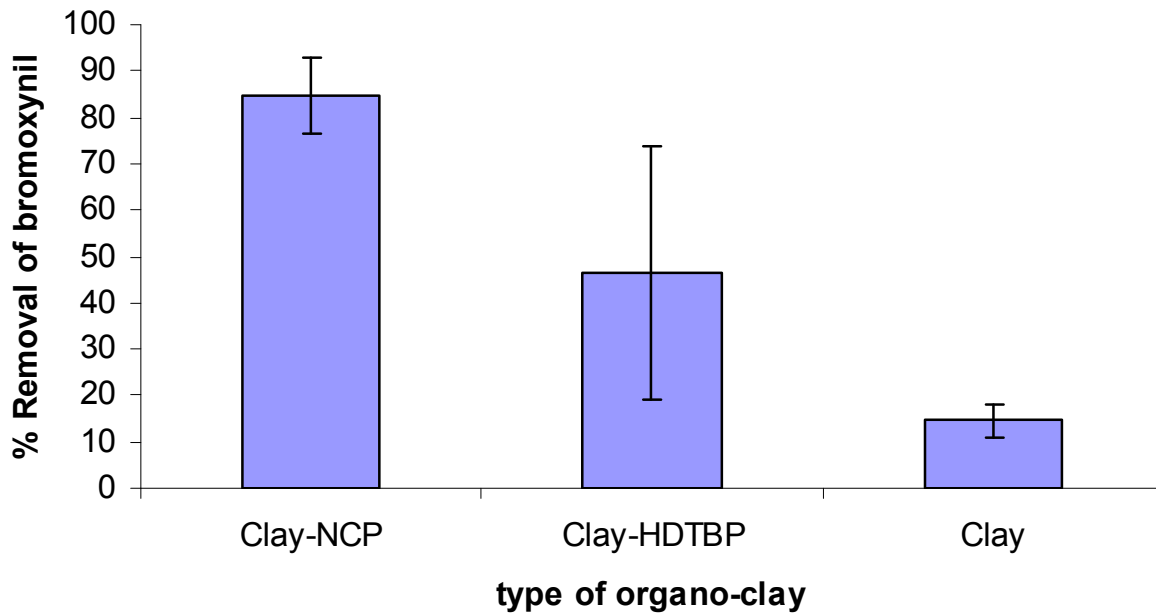


Figure 1. Removal of bromoxynil from water by different organo-bentonites. Error Bars represent standard deviation.

Effects of various concentrations of bromoxynil on the removal process are shown in Figure 2. It is obvious that at low concentration of bromoxynil, the removed amount by using organo-bentonite complexes exceed 90% of bromoxynil from water, whereas at high bromoxynil concentrations (25 mg/l), the removed amount of bromoxynil reduced to 48.02% and 76.57% using Clay-HDTBP or Clay-NCP respectively. Using hydrophilic clay the removed amount of bromoxynil did not exceed 8% and was not affected by the concentration of bromoxynil.

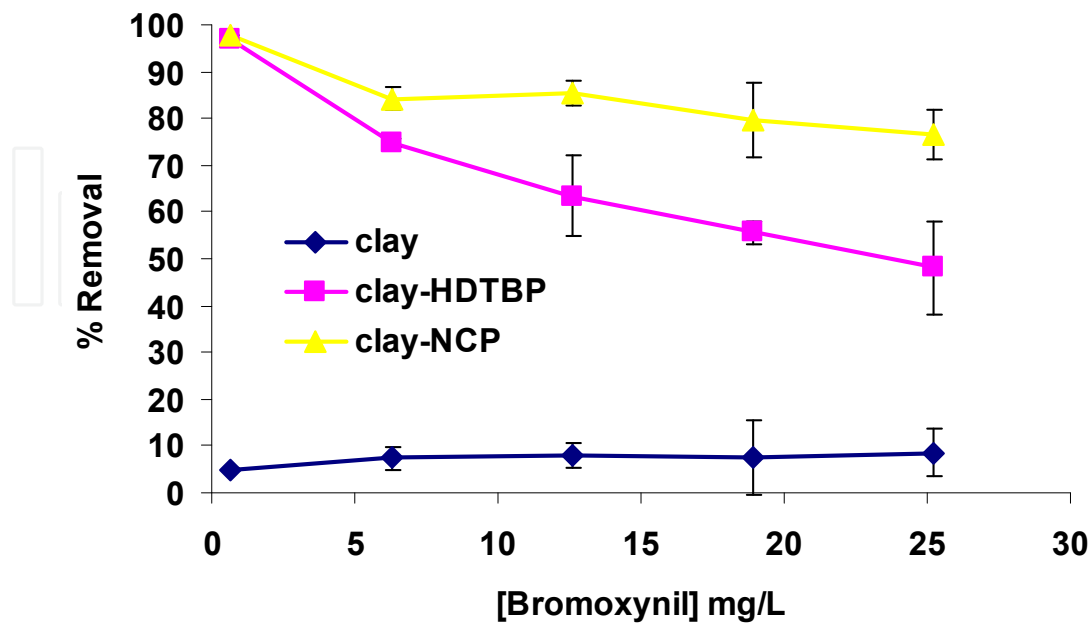


Figure 2. Influence of Bromoxynil concentration in the removal process. Error bars represent standard deviation

The explanation of these results is that at low concentration of bromoxynil the molar concentration of the adsorption sites equal to 0.0096 meq/l. Under these condition, the molar ratio between bromoxynil molecules and the adsorption sites is nearly similar. At a high concentration of bromoxynil the molar ratio between bromoxynil molecules and the adsorption sites tend to increase. Accordingly, the number of free adsorption sites tends to decrease, under this condition the removed amount of bromoxynil tends to decrease. Furthermore, one can realize from the data in Figure 2 that Clay-NCP is more potent than Clay-HDTBP for removal of bromoxynil from water. The explanation of these results is that Clay-NCP contains an aromatic ring in its chemical structure which may enhance the interaction between bromoxynil molecules and Clay-NCP molecules. El-Nahhal et al., [19] demonstrated the efficacy of the chemical structure in enhancing the adsorption of organic molecules from water. Under this condition, hydrophobic interaction between the adsorbed molecules of bromoxynil and those in water may be enhanced. Lagaly (1994) showed similar phenomena for HDTMA.

In addition, using different fractions of organo-bentonite for removing bromoxynil showed optimal removal at low fraction of organo-bentonite complexes (Data not shown). The explanation of these results is that at low fraction of organo-bentonite complex the adsorption sites are diluted in the solution and available for interaction with bromoxynil from water whereas at high concentration of organo-bentonite complexes the percent removal tends to decrease due to possible aggregation of organo-bentonite complexes in the water clay suspension. Accordingly, the availability of free adsorption sites is limited for removal of bromoxynil. Consequently, the concentration of the adsorption site in water should be optimized. It was shown that the best results were obtained at a very diluted organo-Bentonite complexes (Data not shown).

Influence of pH values in the removed amount of bromoxynil from water is shown in Figure 3.

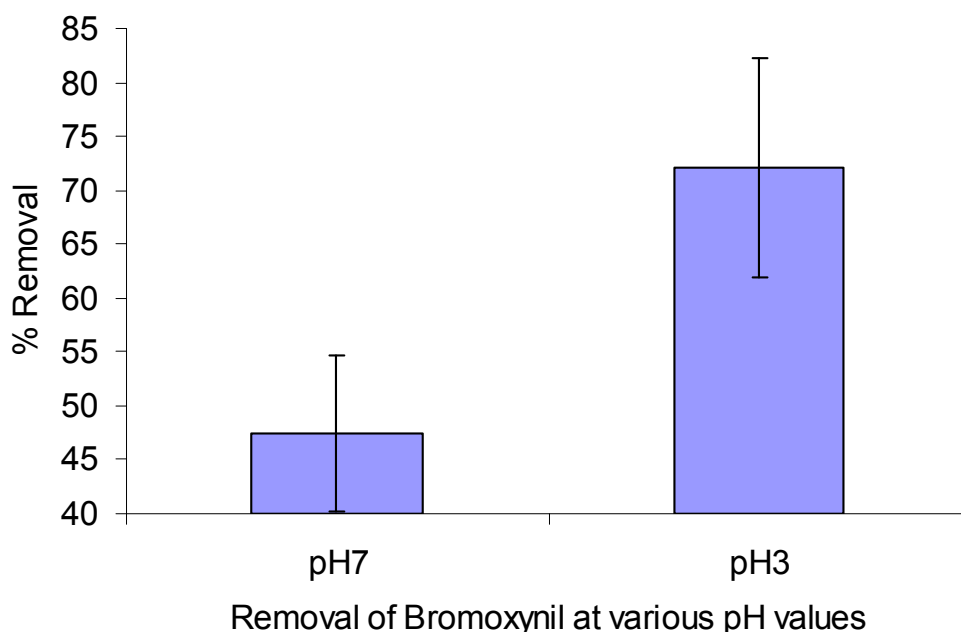


Figure 3. Influence of pH values in the removal of bromoxynil from water by Bentonite-HDTBP. Error bars represent standard deviation

It is obvious that the removed amount of bromoxynil at pH 3 is several times higher than the removed amount at pH 7. The explanation of these results is that bromoxynil has an acid dissociation constant pKa value of 4.06 [20], accordingly the degree of ionization in the solution depends on both the pKa value and the pH of the solution in which it is dissolved, a relation described by the Henderson-Hasselbalch equation for weak acids:

$$pK_a - pH = \log \frac{[\text{nonionized}]}{[\text{ionized}]} \quad (1)$$

Employing Eq 1 at pH 3, one can realize that the nonionized fraction equals to 11.48 times higher than the ionized fraction whereas at pH 7 the nonionized fraction equals to 0.001 of the ionized fraction. As obvious at pH 3 bromoxynil molecules remain in the nonionized form (Hydrophobic form) and adsorbed directly to the organo-bentonite (Figure 3) whereas at pH 7 bromoxynil molecules tend to be ionized (Hydrophilic form) in this case it remains in the solution due to formation on anionic form (Figure 4). This explanation is in accord with the higher removed amount of bromoxynil at pH 3 (Figure 3).

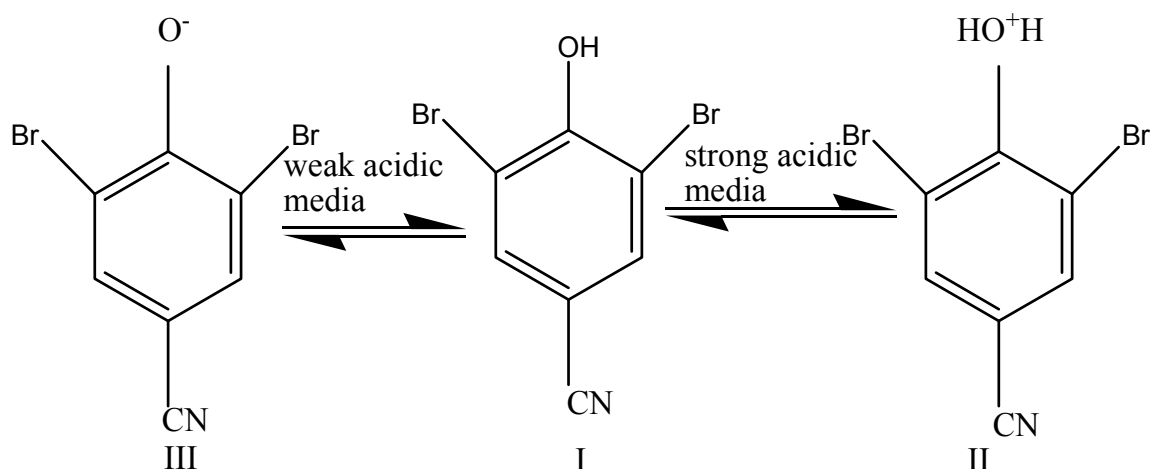


Figure 4. Proposed ionic forms of bromoxynil according to pH values.

The presented results agree with previous reports [21-22] who found high adsorbed amount of bromoxynil in soil and wheat char at low pH.

Removal of bromoxynil at various temperatures are shown in Figure 5. It can be seen that removed amount of bromoxynil is more pronounced at 17 °C than at 40 or 5 °C (Figure 5).

The explanation of these results is that at a low temperature (e.g. 5 °C) the chemical potential of bromoxynil molecules is reduced and the molecules tend to form crystals due to low solubility in water (0.13 g/l, 20 °C). This agrees with the general concept of solubility in chemistry. In contrast, at high temperature the system absorbs heat energy and an increase in the chemical potential may have occurred. This step makes more bromoxynil molecules

available for removal from water due to dynamic mobility in the aqueous solution. The optimal removed amount appears to be at 17 °C.

Extraction experiments using ultrasonic machine showed that nearly the same amount of bromoxynil that removed from water (Figure 1) was extracted from the matrixes used in this study (Data not shown). These results indicate the efficacy of the used matrixes in removing of bromoxynil. These results are in agreement with recent report [23] who showed that bromoxynil was strongly encapsulated in organo-clay complex and used for slow-release formulations under field conditions.

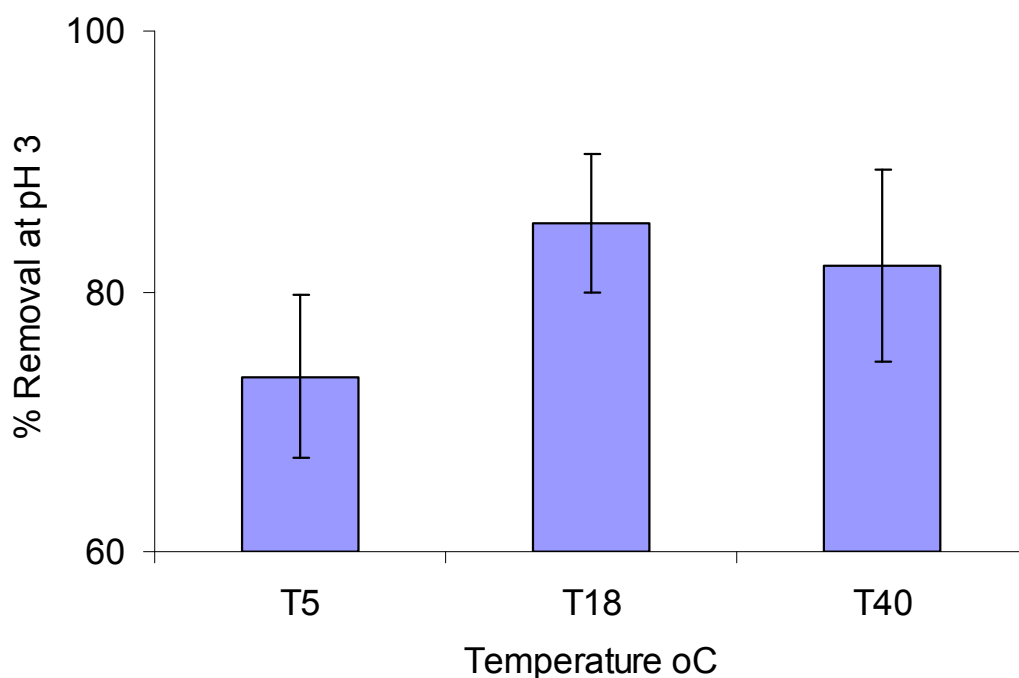


Figure 5. Removal of bromoxynil at different temperatures. Error bars represent standard deviation

4. Concluding remarks

The study reveals that exchanging Bentonite surfaces with organic cations increases their capacity to remove bromoxynil (organic pollutant) from water.. The rationale of this work is that removal of bromoxynil from water can be enhanced by modifying the Bentonite surfaces with NCP and HDTBP. The results showed that highest removed amount of bromoxynil was obtained at pH 3 and at 17 °C (Figures 3, 5). Extraction of bromoxynil from the used matrixes was nearly similar to the amount removed in Figure 1. The environmental relevance of this work emerges from the fact that organo-bentonite complexes can be used to remove organic pollutants from water and develop environmentally acceptable herbicide encapsulation for safe application [24].

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