Original Article

Adsorption of bromoxynil by modified bentonite: influence of pH and temperature

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This study investigates the adsorption behavior of bromoxynil under various pH and temperature conditions. Organo-bentonite complexes were prepared and used as adsorbents for bromoxynil. The concentrations of bromoxynil in equilibrium solution were determined by HPLC. Results showed that bromoxynil was best adsorbed by bentonite surfaces modified with NCP or HDTBP at various loadings, and adsorption was further enhanced by lowering the pH and/or optimizing the temperature of the adsorption reaction. Release of bromoxynil from NCP-, or HDTBP-bentonite- bromoxynil was slower than from raw bentonite-bromoxynil. Organo-bentonite complexes may be suitable materials for designing controlled release formulations of herbicides. ©Pesticide Science Society of Japan

Key words: bromoxynil, adsorption, organo-bentonite, pH, temperature.

Introduction

Bromoxynil is a nitrile herbicide, but its application results in environmental contamination; for instance, it has been detected in atmospheric samples¹⁾, regular water samples²⁾, soil samples³⁾, and in blood specimens⁴⁾. Furthermore, bromoxynil has been reported as a toxic agent to *Chlorella pyrenoidosa* and *Scenedemus obliquus*⁵⁾, important green algae in the ecosystem. Application of current formulations of bromoxynil (emulsion concentrate, and/or suspension concentrate) in the ecosystem may induce species shifts within communities and could affect the structure and function of aquatic communities⁶⁾.

Yang *et al.*⁷⁾ and Sheng *et al.*⁸⁾ evaluated the effect of pH on the adsorption of diuron, bromoxynil, and ametryne by a wheat (*Triticum aestivum* L.) residue-derived black carbon (WC) as compared to a commercial activated carbon (AC), and found that bromoxynil sorption by soil and wheat char was low at approximately pH 7.0.

Baup *et al.*⁹⁾ evaluated the importance of surface diffusivity in pesticide adsorption kinetics using granular versus powdered activated carbon; however, adsorption of bromoxynil by

clay or organo-clay may result in reduced distribution to the environmental components. Very little is known about the effect of pH and temperature on the adsorption of bromoxynil by clay or organo-clay. The reason for using clay or organo-clay in this study was because herbicides are applied directly to soils which contains a high fraction of clay and organic matter, and clay minerals have high cation exchange capacity, making them good porous materials for adsorption. Clay and organo-clay have potential industrial activity in pesticide formulations.

The objectives of this work were to investigate: 1) the adsorptive behavior of bromoxynil by different organo-bentonite complexes; 2) the effect of pH and temperature on adsorption behavior; and 3) release of bromoxynil from organo-bentonite-bromoxynil complex in aqueous solution.

Experimental

1. Materials

Ca²⁺-bentonite clay (M48) has a cation exchange capacity (CEC) of 96 cmol (+) kg⁻¹ (0.96 meq g⁻¹).¹⁰⁾ Organic salts: *N*-cetylpyridinium bromide (NCP⁺Br⁻), *N*-dodecylpyridinium chloride (NDP⁺Cl⁻), *N*-hexadecyl tributylphosphonium bromide (HDTBP⁺Br⁻), and bromoxynil (HPLC grade, 3,5-dibromo-4-hydroxybenzonitrile) were purchased from Sigma Chemical Co. (Germany).

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2. Synthesis of organo-bentonite complexes

The organo-bentonite complexes were synthesized by adding 5 mmol of the solid organic salt to 1 liter of 1% (w/v) aqueous dispersion of M48 under stirring for 3 days¹¹⁾.

3. Adsorption experiments

3.1. Adsorption of bromoxynil by modified clay with different organic cations and different loadings

Bromoxynil stock solution was prepared by dissolving 31 mg in 2–3 ml methanol and diluting to 1 liter with deionized water. In this experiment, a fixed amount of bromoxynil (50 mg/g organo-bentonite complex) was diluted in 25 ml water at pH 3 and added to various glass centrifuge tubes containing 10 mg organo-bentonite with different loadings of organic cations (mmol organic cation/g bentonite). The tubes were shaken for 48 hr at 17°C and then the supernatants were collected by centrifugation at 20,000 *g*. The remaining concentration of bromoxynil in the supernatants was determined by HPLC as below.

3.2. Adsorption of bromoxynil by modified clay with HDTBP at 2, 4, 24 and 48 hr at pH 7 and 17°C

In this experiment, a fixed amount of bromoxynil (50 mg/g organo-bentonite complex) was added to various glass centrifuge tubes containing 10 mg HDTBP-bentonite and rotary shaken for the above time. The supernatants were then collected by centrifugation at 20,000 *g*. The remaining concentration of bromoxynil in the supernatants was determined by HPLC as below. Glass centrifuge tubes containing the same concentration of bromoxynil without HDTBP-bentonite were used as control samples and shaken for the above time to evaluate the stability of bromoxynil.

3.3. Adsorption isotherms of bromoxynil

Appropriate aliquots of the aqueous stock solution of bromoxynil were diluted with deionized water (pH 7) to 25 ml and added to 5 mg organo-bentonite in 30 ml glass centrifuge tubes at 17°C. The concentration of bromoxynil ranged between 1.2–31 mg/l. The dispersions were kept under continuous rotary agitation for 48 hr. The supernatant was then separated by centrifugation at 20,000 *g* for 0.5 hr. To measure the effect of temperature on the adsorption of bromoxynil, the adsorption experiment was maintained at 5, 17 and 40±2°C using NCP-bentonite complex at pH 3.

3.4. Control samples

Control samples were made by performing the same adsorption experiments under the same conditions without adding organo-bentonite to each tube. The supernatant was separated by centrifugation at 20,000 *g* for 0.5 hr and bromoxynil concentration in each tube was determined by HPLC as described below.

4. Effect of pH on adsorption

The stock solution of bromoxynil and the dilutions were brought to pH 3 by the addition of a few drops of acetic acid. This was possible because the adsorption solution was so small (25 ml). At pH 7, the adsorption experiments were performed using deionized water as described above using HDTBP-bentonite complex at 17°C.

5. HPLC measurements of bromoxynil

The concentrations of bromoxynil in the supernatants were determined by Waters 717 HPLC with a UV detector (detection wavelength 283 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 amount of bromoxynil adsorbed was calculated from depletion of the bromoxynil concentration in aqueous solutions.

6. Synthesis of organo-bentonite-bromoxynil complexes

Organo-bentonite-bromoxynil complexes were prepared as previously described¹¹⁾ and used as the formulation model. The organo-bentonite complexes used in this study contain organic cations at 25–43% of the cation exchange capacity of bentonite. In this case, the clay mineral becomes sufficiently hydrophobic but the organic cations are not densely packed in the interlayer space and provide more adsorption sites for the herbicide.

7. Release of bromoxynil from organo-bentonite-bromoxynil complexes

Release experiments were performed using a funnel experiment¹²⁾ to investigate how slow the release process is. In this procedure, 0.2 g organo-bentonite-bromoxynil complex containing 5% bromoxynil was mixed thoroughly with 50 g oven dried sandy soil in a glass beaker and placed in a Buckner funnel containing tissue paper. The sand in each Buckner funnel was eluted with 500 ml distilled water added as 10 ml each 15 min. Distilled water and water brought to pH 3 with a few drops of acetic acid were used separately in the experiment. Only the results at pH 3 are presented. The eluted water was collected in a 50 ml conical flask. About 1 ml of each sample was centrifuged at 20,000 *g* for 0.5 hr and analyzed by HPLC as mentioned above.

8. 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).

Results and Discussion

The cationic quaternary ammonium/phosphonium salts used in this study are solid materials at room temperature, and surface-active agents (surfactants), because each molecule has a non-polar hydrocarbon group and an ionic, polar component. 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 identical (data not shown), whereas as the added concentration increased (>0.5 mmol/g), the extent of adsorption became a function of the size and shape of the surfactant. Large organic cations can effectively displace inorganic ions, such as Ca^{2+} and Na^{+} , from the mineral surfaces of clay by ion exchange¹³.

Case control results of bromoxynil stability and adsorption in the glass of centrifuge tubes showed no changes in bromoxynil concentrations at the beginning and end of the experiments, indicating the stability of bromoxynil and that no adsorption occurred on the glass wall of the centrifuge tube (data not shown).

The adsorbed amounts of bromoxynil by raw bentonite or modified bentonite with NDP, NCP and/or HDTBP were 6.8 ± 2.5 , 8.54 ± 3.74 , 38.37 ± 0.01 , and 55.87 ± 0.85 mg/g, respectively. The experiments were all performed at pH 7 and 17°C . Statistical analysis showed significant differences between adsorption on raw bentonite and bentonite modified with NCP or HDTBP, p -value=0.01, whereas no difference between adsorption by bentonite modified with NDP and raw bentonite was observed, p -value=0.21.

The largest adsorbed amount of bromoxynil was observed on bentonite modified with HDTBP. The explanation for these results is that low adsorption on raw bentonite is due to its hydrophilic surface and the hydrophobic nature of bromoxynil, whereas modification of bentonite surfaces with HDTBP may result in the formation of a microscopic organic phase on the surface, as in hexadecyltrimethyl ammonium-smectite¹⁴. This may enhance the partitioning of bromoxynil in HDTBP-bentonite. It was reported that the organic phase formed by hexadecyltrimethyl ammonium (HDTMA) on montmorillonite surfaces acts as a solubilizing (partitioning) medium to remove non-ionic organic compounds from water¹⁵.

The adsorbed amount of bromoxynil (mg/g organo-bentonite complex) with HDTBP-bentonite at 2, 4, 24, and 48 hr was 20.49 ± 0.02 , 19.58 ± 0.52 , 22 ± 0.87 , and 20.08 ± 0.37 , respectively. Statistical analysis showed no significant difference among cases, and p -values associated with the t -test were >0.06 . These results are in agreement with previous results by El-Nahhal and Safi¹⁶.

The effects of various loadings of organic cations on bentonite surfaces on improving the adsorption of bromoxynil are shown in Fig. 1. It was clear that the adsorbed amount of bro-

Fig. 1. Adsorption of bromoxynil on bentonite modified with *N*-cetylpyridinium (NCP-M48), *N*-dodecylpyridinium (NDP-M48) and hexadecylterabutyl phosphonium (HDTBP-M48) at various loadings (mmol/g). Bromoxynil and organo-bentonite concentrations are 20 mg/l and 0.4 g/l respectively. Bars represent standard deviation.

moxynil increased as the organic loading increased on bentonite surfaces. The explanation for these results is similar to above.

Figure 2 illustrates the adsorption isotherms of bromoxynil on various organo-bentonite complexes at pH 7. As expected, bromoxynil was poorly adsorbed on raw bentonite (M48), whereas bentonite modified with NDP, NCP, or HDTBP significantly enhanced the adsorbed amount. The adsorption of bromoxynil increased as its concentration in the equilibrium solution increased. The explanation for these results is similar to above. Adsorption of bromoxynil followed the sequence bentonite-HDTBP > bentonite-NCP > NDP-bentonite > bentonite.

These results indicate that bromoxynil adsorption by organo-bentonite is dependent on the molecular size and chemical structure of the organic cation pre-adsorbed on bentonite surfaces, as previously suggested in other cases¹⁷. These results are in agreement with El-Nahhal¹⁸ who emphasized the influence of the partial saturation of bentonite surfaces ($\sim 60\%$ of the cation exchange capacity of bentonite) and the size of the organic cation pre-adsorbed by bentonite. In addition, the author showed that π - π interaction of the phenyl rings of the herbicide and the organic cation pre-ad-

Fig. 2. Adsorption isotherms of bromoxynil on Bentonite modified with NDP0.6, NCP0.8, or HDTBP0.11; The number close to NDP NCP or HDTBP indicates the concentration (mmol/g) of organic cation in Bentonite. Error bars represent standard deviation.

sorbed by bentonite is reduced at a larger size of organic cation or at full saturation of the bentonite surfaces.

Furthermore, the shape of the isotherms was similar in all cases. According to Gile *et al.*¹⁹⁾ classification, isotherms of bromoxynil 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 (Figs. 2, 3, 5), which indicated no strong competition for the adsorption sites between the solvent (water) and bromoxynil molecules on organo-bentonite complexes. This suggests that bromoxynil 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 Fig. 2 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 bromoxynil mg/l, 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

Fig. 3. Effect of pH on the adsorption isotherms of bromoxynil on Bentonite modified with HDTBP at 17°C. Bares represent standard deviation.

raw bentonite is several times lower than on bentonite-NCP0.8 and bentonite-HDTBP, indication the high affinity of bromoxynil to bentonite-HDTBP.

As the adsorption of bromoxynil on bentonite-HDTBP was quite high compared to others, we used this complex as the optimum model for further experiments.

Figure 3 shows the adsorption isotherms of bromoxynil on bentonite-HDTBP at various pH values. Bromoxynil has an acid dissociation constant of 8.71×10^{-5} and is mostly neutral at pH <4.06, becoming deprotonated (anionic) at pH >4.06.²⁰⁾ Accordingly, the adsorbed amount of bromoxynil obtained at pH 3 is higher than the adsorbed amount obtained at pH 7 (Fig. 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, bromoxynil molecules are mostly neutral and/or protonated, and in this case they may be adsorbed either as cations on hydrophilic sites of the organo-bentonite surface or as neutral molecules on hydrophobic sites. At pH 7, the majority of bromoxynil molecules are partially negative in equilibrium with the neutral form (Fig. 4). In this case, only neutral molecules are adsorbed on the hydrophobic sites of organo-bentonite surfaces, and the anionic forms stay in solution; accordingly, low adsorbed amounts of bromoxynil were observed. In addition, electronic repulsion between the anionic form of bromoxynil and the negatively charged bentonite surfaces or the higher solubility of the anion in water were also reasons for

Table 1. Adsorption parameters of bromoxynil on different organo-bentonite calculated from Freundlich equation

Adsorbent name	K	n	r^2
Bentonite (M48)	0.29	0.88	0.9959
Bentonite-NDP0.6	0.43	0.83	0.9567
Bentonite-NCP0.8	29.1	2.05	0.9849
Bentonite-HDTBP0.11	52.12	3.88	0.9576

Fig. 4. Effect of pH on the ionic status of bromoxynil, I, II, and III represent the neutral, cationic, and anionic forms at pH 4.06, 3, and 7 respectively.

Fig. 5. Effect of temperature on the adsorption isotherms of bromoxynil on bentonite modified with NCP. The experiment was maintained at pH 3. Bars represent standard deviation.

the reduced adsorption.

The presented results agree with previous reports^{7,8)} that found a high adsorbed amount of bromoxynil in soil and wheat char at low pH. It has been shown that the interaction of organic molecules with modified clays, and/or soil organic matter occurred via portioning, according to the octanole/water-partitioning coefficient¹⁶⁾. Furthermore, the shape of the isotherm tends to be L-type¹⁷⁾ and adsorption occurs as the Langmuir type at various pH values, due to changes in the electronic form of bromoxynil as a result of pH changes.

Adsorption of bromoxynil is more pronounced at 17°C than at 5°C (Fig. 5) because, at a low temperature, the chemical potential of bromoxynil molecules is reduced and the molecules tend to form crystals due to their low solubility in water (0.13 g/l, 20°C). This agrees with the general concept of solubility in chemistry. In contrast, at high temperatures, the system absorbs heat energy and an increase in the chemical potential of the adsorption reaction may occur. This step makes more bromoxynil molecules available for adsorption due to dynamic mobility in the aqueous solution; accordingly, high adsorption is observed. The optimal adsorption appears to be at 17°C as the K value is higher, indicating adsorption affinity. As shown in Fig. 5, the adsorbed amount of bromoxynil at 17°C is higher than at 40°C, but statistical analysis showed no significant differences, $p=0.05$; this was also clear from the overlapping error bars of the isotherms at 17°C and 40°C. This supports the suggestion that optimal adsorption occurred at temperature 17°C; however, statistical analysis of adsorption data at 5°C and 17°C showed significant differences at equilibrium concentrations above 2 mg/l (Fig. 5); p -values with these analysis were <0.02 .

Changes in molar free energy (ΔG°) of the adsorption reaction of bromoxynil at different temperatures were calculated using the following equation²¹⁾:

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

where, ΔG° is the molar free energy change (Kcal/mol), R is

Fig. 6. Release of bromoxynil from different organo-bentonite formulations using deionized water adopted at pH 7. Bromoxynil concentration in all organo-Bentonite complexes is 0.05 g/g. Bars represent standard deviation.

the gas constant (1.986 cal/(K 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 5°C and 17°C from distilled water were $-0.8376 \pm (0.03)$ Kcal/mol and $-1.1562 \pm (0.17)$ Kcal/mol, respectively. These results are in accordance with the data in Fig. 5. These values are within the expected range for physical adsorption. Analysis of variance between the calculated free energy at 5°C and 17°C gave a p -value of 0.0002, whereas there was no significant difference between the calculated free energy at 17°C and 40°C, p -value=0.36.

The release of bromoxynil from different organo-bentonite complexes at pH 3 is shown in Fig. 6. It is evident that upon application of 50 ml water (first washing) 53% of the initial bromoxynil concentration was released from raw bentonite-bromoxynil complex (M48), whereas 8% and 4% bromoxynil concentrations were released from NCP-bentonite-bromoxynil and HDTBP-bentonite-bromoxynil complexes, respectively. Further application of eluting water up to 500 ml resulted in the further release of bromoxynil up to 87%, 17% and 9% from raw bentonite-bromoxynil (M48), NCP-bentonite-bromoxynil and HDTBP-bentonite-bromoxynil complexes, respectively; thus, the release of bromoxynil from organo-bentonite-bromoxynil complexes was significantly slower than from raw bentonite. This was because the release of bromoxynil from organo-bentonite-bromoxynil complexes is controlled by the binding coefficients, (K_d) values, which are very high for the organo-bentonite-bromoxynil and low for the raw-bentonite-bromoxynil complex (Table 1). These results are in agreement with a previous report²²⁾, which found that herbicide evaporation was controlled by binding coefficients. These results are in accordance with the adsorption data (Figs. 2–4).

Concluding Remarks

This study reveals that exchanging bentonite surfaces with organic cations increases bromoxynil adsorption. The rationale for this work is that the adsorption of bromoxynil on bentonite can be enhanced by modifying bentonite surfaces with NDP, NCP, and HDTBP. The findings showed that the highest adsorbed amounts were obtained at pH 3 and at 17°C (Fig. 4). The release of bromoxynil was very slow from organo-bentonite complexes (Fig. 6). The environmental relevance of this work is that organo-bentonite complexes can be used to develop environmentally acceptable herbicide formulations for safe application¹²⁾, controlled release formulations of bromacil²³⁾, and the removal of organic pollutants from water²⁴⁾.

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