

Studies on removal of metribuzin, bromacil, 2,4-D and atrazine from water by adsorption on high area carbon cloth

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Abstract

The removal of pesticides such as metribuzin, bromacil, 2,4-D and atrazine from aqueous solutions was studied by adsorption on high area carbon cloth. The adsorption process was followed by in situ UV-spectrophotometric technique in a specially designed adsorption cell. Spectroscopic data of the pesticides were determined in separate experiments. The extent of adsorption was quantified by calculating the amount of adsorbate adsorbed per unit area of the carbon cloth and the percentage coverage at the carbon-cloth surface. The order of extent of adsorption of the pesticides studied was found as metribuzin < 2,4-D < bromacil < atrazine. The adsorption process was found to follow a first-order kinetics and the rate constants were determined. The competitive adsorption of pesticides was also examined by carrying out the adsorption process from a solution of equimolar mixture of bromacil and metribuzin.

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1. Introduction

The contamination of surface and ground water by pesticides is an important problem that the scientists are dealing with over the years. Many of the studies toward the solution of this problem involve determination of adsorptive behavior of pesticides on various adsorbents such as kerolite, Al-pillared clay, bentonite, lignin, quartz, calcite, kaolinite and α -alumina [1–5]. Activated carbon materials have a special place among the adsorbents, as they are known to be capable of adsorbing various organic compounds for a long time. The number of studies on adsorption of pesticides on carbon materials from aqueous solution has increased in recent years. Pelekani and Snoeyink [6] reported the adsorption of atrazine on activated carbon fibers, Yang et al. [7] studied the phenoxyacid herbicide adsorption on granular activated carbon, Hu et al. [8] examined the adsorptive characteristics of inorganic aromatic pesticides on powdered activated carbon and Hoda and Ayranci [9] studied adsorption kinetics of bentazon and propanil

at the carbon felt. More attractive carbon materials are now available with large specific areas on the order of 2000–2500 m² g⁻¹. Felts or cloth are preferable as they have good mechanical and structural integrity and are thus more suitable than materials based on powders. At high area porous materials such as carbon cloth or carbon felt, the diffusion limitation to adsorption is minimized since the material behaves as quasi-three-dimensional [10]. Another advantage of high-area carbon material as adsorbent is its functionality for accumulation of larger amount of impurities with the possibility of subsequent desorption into a vessel of smaller volume where some other localized, possibly chemical destructive process can be applied. This provides a procedure for regeneration of the active surface. Recently, the use of high-area carbon-cloth electrodes has been investigated for adsorption and electrosorption behavior of various adsorbates such as inorganic S-containing anions [11], ethylxanthate and thiocyanate [12], phenol, phenoxide and chlorophenols [13] and some aromatic heterocyclic compounds [14] in relation to waste-water purification.

Most of the adsorption studies from aqueous solutions involve the measurement of concentration of the adsorbate as a function of time, amount of adsorbent, and/or temperature. Therefore the concentrations of adsorbate should

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be followed by a suitable, practical, fast responding and preferably non-destructive in situ method. In this respect, optical absorbance measurements provide a convenient way for molecules absorbing in UV–vis region. In situ measurements also allow the study of kinetics of the adsorption process. Such a method was originally proposed by Conway et al. [15] and successfully applied to adsorption studies in our previous studies [9–14].

The purpose of the present work is to examine the adsorption behavior of some pesticides such as metribuzin, bromacil, 2,4-D and atrazine on high area carbon cloth by in situ UV spectroscopy. This method was selected to follow the adsorption since the four pesticides are capable of absorbing UV light. Conversely, the UV light absorbability is one of the reasons for selecting the pesticides studied. Other main reasons for the selection of the four pesticides are the sufficient solubility in water to follow their adsorption by the proposed method and the necessity to remove from water due to their toxicity.

2. Materials and methods

2.1. Materials

The carbon cloth used in the present work was obtained from Spectra Corp. (MA, USA) coded as Spectracarb 2225, having a specific area of $2500 \text{ m}^2 \text{ g}^{-1}$. The pesticides metribuzin (4-amino-6-*tert*-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-5-one), bromacil (5-bromo-3-*sec*-butyl-6-methyluracil), 2,4-D (2,4-dichlorophenoxyacetic acid) and atrazine (2-chloro-4-ethylamino-6-isopropylamine-s-triazine) were obtained from Riedel-de Haen (Germany). Deionized water was used in adsorption experiments.

2.2. Treatment of the carbon cloth

The carbon-cloth material was found [11] to provide spontaneously a small but significant quantity of ions into the conductivity water used, probably due to its complex structure originating from its somewhat unknown proprietary preparation procedure. A deionization cleaning procedure was therefore applied, as described previously [11] to avoid desorption of ions during the adsorption measurements.

In this procedure, a carbon-cloth sample was placed in a flow-through washing cup and eluted with 5 L of warm (60°C) conductivity water in a kind of batch operation for 2 days with N_2 bubbling in order to avoid possible adsorption of CO_2 that might have been dissolved in water. The out-flow water from each batch was tested conductometrically for completeness of the washing procedure. The washed carbon-cloth modules were then dried under vacuum at 120°C and kept in a desiccator for further use. The carbon cloth was cut to desired dimensions (about $0.5 \text{ cm} \times 1.5 \text{ cm}$), weighed accurately and attached to a short Pt wire for introduction into the adsorption cell.

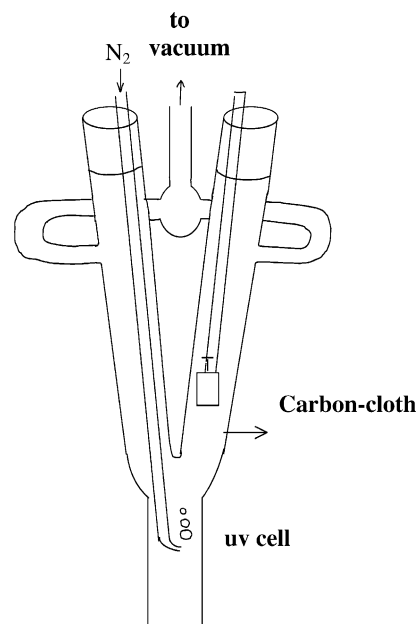


Fig. 1. Diagram of the adsorption cell.

2.3. Adsorption cell

A special cell was designed to carry out the adsorption studies and simultaneously to make in situ concentration measurements by means of UV absorption spectrophotometry. The cell (Fig. 1) was V-shaped with one arm containing the carbon cloth attached to a short Pt wire and the other arm containing a thin tube through which N_2 gas was passed for the purposes of mixing and eliminating any dissolved CO_2 . The two arms were connected to a glass joint leading to a vacuum pump at the upper part of the V-shaped cell in order to provide the opportunity for initial outgassing of the carbon adsorbent, and the cell and solution. A quartz spectrophotometer cuvette was sealed to bottom of the adsorption cell.

2.4. Optical absorbance measurements

A Shimadzu 160A UV–vis spectrophotometer was used for optical absorbance measurements. The absorbance measurements were conducted in situ during the study of the adsorption process as follows. A piece of carbon cloth accurately weighed and pre-wetted for more than a day, was attached to the Pt wire sealed to the tip of a glass tubing and placed in one arm of the adsorption cell described above. In all experiments, the size and weight of the carbon cloth was kept as constant as possible (about $18.0 \pm 0.1 \text{ mg}$). Its weight was accurately measured and recorded each time for calculation of fractional coverage, θ , by the adsorbate or the amount of adsorption per unit area of the carbon cloth. The idea of using pre-wetted carbon cloth originates from our previous findings that pre-wetting enhances the adsorption process [11,12].

The whole cell including the carbon cloth was first evacuated to remove all air in the pores of the carbon cloth. A known volume of water was introduced to the cell from a burette fitted to one of the arms of the cell by a glass joint. Further evacuation was applied after adding the water to ensure that all air in the pores had been removed and water had attained access to the whole carbon surface. The vacuum was then released and the burette removed.

The sliding door of the sample compartment of the spectrophotometer was left half-open and the quartz cuvette fixed at the bottom of the adsorption cell (which now contained the carbon cloth and water) was inserted into the front sample compartment. A Teflon tube connected to the tip of a thin N₂-bubbling tube was lowered down the UV cell to a level just above the light path to provide effective mixing.

Finally, a calculated volume of relatively concentrated solution of individual adsorbates was accurately added from the arm of the adsorption cell containing the N₂-bubbling tube using a micrometer burette. Then, quickly, an opaque curtain was spread above the sample compartment of the spectrophotometer, over the cell, to prevent interference from external light.

The program for monitoring the absorbance at the specific wavelength of maximum absorbance pre-determined by taking the whole spectrum of each pesticide was then run on the built-in microcomputer of the spectrophotometer. Absorbance data was recorded in programmed time intervals of 1 min over a period of 125 min.

Absorbance data were converted into concentration data using calibration relations pre-determined at the wavelength of interest for each pesticide.

Adsorption study was repeated on duplicate or triplicate samples of carbon-cloth pieces. The absorbance values were reproducible within 2% for duplicate or triplicate samples.

3. Results and discussion

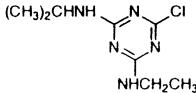
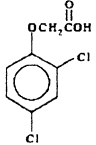
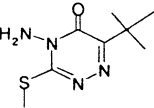
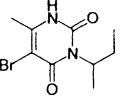
3.1. Absorption characteristics and calibration data for the pesticides

The observed wavelengths of maximum absorption (λ_{\max}) for the pesticides studied are given in Table 1. Separate calibration experiments were run to determine the required molar absorptivities (ϵ) according to the Lambert–Beer law using aqueous solutions of pure pesticides. Absorbance versus concentration data for each compound were treated by linear regression analysis. All the spectral calibration data for the pesticides studied are included in Table 1.

3.2. Adsorption behavior of individual pesticides

In order to make a comparative study for the adsorption of individual pesticides; the initial pesticide concentration and the weight of carbon cloth used were kept almost the same in the adsorption experiments on each pesticide. The changes in pesticide concentration with time during the adsorption at the pre-wetted carbon cloth are shown in Fig. 2 collectively for all the pesticides studied. On the overall, there is about a 10-fold decrease in the pesticide concentration in the aqueous solution upon adsorption onto the carbon cloth over 125 min. This observation is important in relation to water treatment for removal of impurities. The adsorption seems to start with the same rate for all four pesticides. However, a clear distinction can be seen in the extent of adsorption when the plateau is approached in the concentration versus time plot at about 125 min of adsorption. The increasing order of the extent of adsorption at this point is metribuzin < 2,4-D < bromacil < atrazine. The differences in the extent of adsorption of pesticides at 125 min are small but significant. These small differences should origi-

Table 1
The spectral and calibration data for the pesticides studied

Pesticide	Structure	λ (nm)	ϵ (a.u. cm ⁻¹ M ⁻¹)	Regression coefficient
Atrazine		223 (λ_{\max})	37,932	0.9998
2,4-D		229 (λ_{\max})	8,426	0.9995
Metribuzin		213 (λ_{\max}) 277 293 (λ_{\max})	10,191 5,748 8,147	0.9998 0.9999 0.9999
Bromacil		210 (λ_{\max}) 277 (λ_{\max}) 293	9,709 7,192 3,752	0.9981 0.9970 0.9977

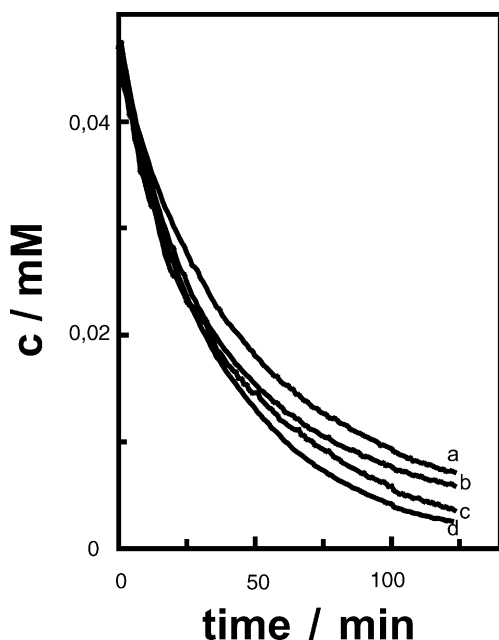


Fig. 2. Adsorption behaviors of (a) metribuzin (b) 2,4-D (c) bromacil, and (d) atrazine on the carbon cloth from aqueous solutions having an initial concentration of 4.69×10^{-5} M. The carbon cloth used in each adsorption experiment was 18.0 ± 0.1 mg.

nate from structural effects of the adsorbates. However, it is difficult to analyze these structural effects since the structures of the pesticides (Table 1) are not closely related. Two of them, 2,4-D and atrazine have aromatic rings with quite different substituents. Metribuzin and bromacil also have a ring structure but again with different substituents. A more quantitative comparison can be made in the extent of adsorption of these compounds by introducing two related terms, the amount of adsorbate adsorbed per unit area of the carbon cloth, M , given by Eq. (1) and the percent coverage at the carbon-cloth surface, θ , given by Eq. (2);

$$M = \frac{(c_0 - c_t)V}{2500m} \quad (1)$$

$$\theta = \frac{[(c_0 - c_t)VN_A 100]}{(4 \times 10^{19} 2500 m)} \quad (2)$$

Table 2

M and θ values defined by Eqs. (1) and (2) at 125 min of adsorption, first-order rate constants and the regression coefficients for the adsorption of the pesticides studied

Pesticides	c_0 (mol L ⁻¹)	M (10 ⁻⁵ mol per meter square carbon cloth)	θ	k (min ⁻¹)	Regression coefficient
Metribuzin	4.69×10^{-5}	1.76	0.026	0.015	0.9995
2,4-D	4.69×10^{-5}	1.81	0.027	0.016	0.9900
Bromacil	4.69×10^{-5}	1.91	0.029	0.020	0.9983
Atrazine	4.69×10^{-5}	1.98	0.030	0.024	0.9995
Metribuzin (in equimolar mixture with bromacil)	1.44×10^{-5}	4.41	0.66		
Bromacil (in equimolar mixture with metribuzin)	1.44×10^{-5}	5.88	0.088		

where c_0 and c_t are the concentrations of the solutions at the beginning and at a specific time during the adsorption process, respectively. V is the volume of the solution, m the weight of the carbon-cloth module and N_A Avogadro's number. The calculations are based on the known specific surface area of $2500 \text{ m}^2 \text{ g}^{-1}$ for the carbon cloth provided by the manufacturer, corresponding to an approximate value of 4×10^{19} carbon sites per square meter of the surface determined by the atomic radius of carbon but dependent on the actually unknown geometry of surface carbon-atom packing.

The M and θ values calculated at 125 min of adsorption are given in Table 2 for the pesticides studied. The above mentioned order of increasing extent of adsorption from metribuzin to atrazine can clearly be seen from M and θ values. It is important to note that the specific surface area of carbon cloth is so large that only a very small percentage is covered even after 125 min of adsorption.

3.3. Kinetics of adsorption

The adsorption data of the four pesticides over 125 min were treated according to first-order kinetics. Excellent linear lines obtained for $\ln c$ versus time plots as indicated by regression coefficients which were very close to one (Table 2) support the assumption of first-order kinetics for the adsorption process. The rate constants and the corresponding regression coefficients are included in Table 2. The rate constants for the adsorption of pesticides follow the order observed for the extent of adsorption at 125 min of adsorption as discussed earlier.

As noted previously [14], adsorption of an organic solute from solution at a carbon or metal interface requires desorption of solvent molecules initially present at the surface. The adsorption process is therefore a substitutional one. Hence, the kinetics of the adsorption will be determined, in part, by the kinetics or activation energy for desorption of solvent water initially present. This, in turn, will be influenced by the two-dimensional density of functional groups on the carbon surface and thus hydrophilicity or hydrophobicity of that surface.

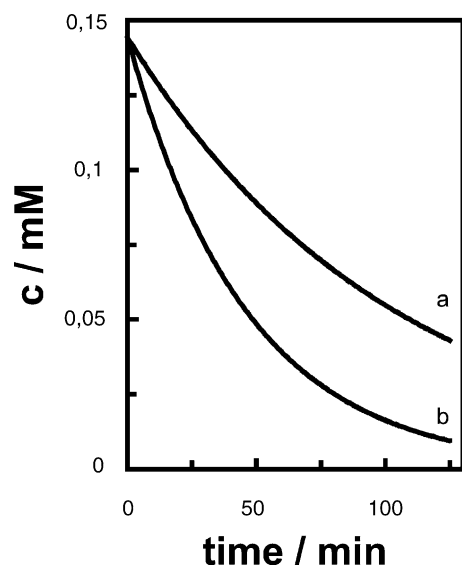


Fig. 3. Adsorption behavior of an equimolar mixture of (a) metribuzin and (b) bromacil on carbon cloth. Initial concentration of each component in the mixture was 1.44×10^{-5} M and the carbon cloth used for the adsorption was 18.0 mg.

3.4. Examination of competitive adsorption

In order to examine the competitive adsorption of pesticides, adsorption from an equimolar mixture of bromacil and metribuzin on the carbon cloth was studied. During this study, simultaneous concentration determination was achieved spectrophotometrically by recording the total absorbances at two wavelengths, 277 and 293 nm, the former being the absorption maximum of bromacil and latter being the absorption maximum of metribuzin (Table 1). The total absorbance at 277 nm, $A^{277}(\text{total})$, can be given by

$$A^{277}(\text{total}) = \varepsilon^{277}(\text{metribuzin})c(\text{metribuzin}) + \varepsilon^{277}(\text{bromacil})c(\text{bromacil}) \quad (3)$$

and at 293 nm $A^{293}(\text{total})$, can be given by

$$A^{293}(\text{total}) = \varepsilon^{293}(\text{metribuzin})c(\text{metribuzin}) + \varepsilon^{293}(\text{bromacil})c(\text{bromacil}) \quad (4)$$

where ε is the molar absorptivity of the pesticide indicated in parenthesis at the wavelength indicated as a superscript and c is the concentration of the pesticide indicated in parenthesis. Since 1 cm spectrophotometer cuvette was used in the measurements, the light pathlength does not appear in the above equations. ε values determined from calibration experiments with the individual pesticides are given in Table 1. Simultaneous solutions of Eqs. (3) and (4) give concentrations of metribuzin and bromacil in the mixture.

The results of the adsorption from equimolar mixture of bromacil and metribuzin are presented in Fig. 3. The general adsorption behaviors of both components in the mixture resemble the behaviors they show when they were alone in

the solution as presented in Fig. 2. The M and θ values defined by Eqs. (1) and (2) calculated at 125 min of adsorption for each component in the mixture are given in Table 2. The strikingly higher M values for the adsorption of metribuzin and bromacil from the mixture than those for the adsorption of each component from their individual solutions result from the higher initial concentrations used in the adsorption experiment of the mixture. However, the effect of presence of a second pesticide in the solution on the extent of adsorption of each pesticide can be examined by comparing the ratio of M values of bromacil to metribuzin for adsorptions from solutions of each pesticides when they were alone and from solutions of equimolar mixture of the two pesticides. This ratio is 1.08 for the former and 1.33 for the latter case. This shows that the greater extent of adsorption of bromacil than metribuzin from individual solutions increases by about 30% when the adsorption is carried out from a solution of equimolar mixture. The preferential adsorption of bromacil probably retards the adsorption of metribuzin in the same mixture to a certain extent. Since the adsorptions of the two pesticides are found to be somewhat affected from each other, first-order kinetics was not applied for the adsorption of each component in the mixture.

4. Conclusion

The adsorption of pesticides at the carbon cloth could be followed by in situ UV-spectroscopy. It was found that carbon cloth having large specific area is a good adsorbent for the removal of pesticides from aqueous solutions. Approximately 10-fold decrease in pesticide concentration of aqueous solution was achieved under experimental conditions described earlier. The order of the extent of the adsorption of four pesticides studied was found as metribuzin < 2,4-D < bromacil < atrazine. The adsorption of pesticides was found to follow a first-order kinetics.

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References

- [1] E. Gonzalez-Pradas, M. Socias-Viciana, M. Saifi, M.D. Urena-Amate, F. Flores-Cespedes, M. Fernandez-Perez, M. Villafranca-Sanchez, *Chemosphere* 51 (2003) 85–93.
- [2] I.K. Konstantinou, T.A. Albanis, D.E. Petrakis, P. Pomonis, *Water Res.* 34 (2000) 3123–3136.
- [3] E. Bojemueller, A. Nennemann, G. Lagaly, *Appl. Clay Sci.* 18 (2001) 277–284.

- [4] J. Ludvik, P. Zuman, *Microchem. J.* 64 (2000) 15–20.
- [5] L. Clausen, I. Fabricius, L. Madsen, *J. Environ. Qual.* 30 (2001) 846–857.
- [6] C. Pelekani, V.L. Snoeyink, *Carbon* 38 (2000) 1423–1436.
- [7] M. Yang, J. Hubble, A.D. Lockett, R.R. Rathbone, *Water Res.* 31 (1997) 2356–2362.
- [8] J. Hu, T. Aizawa, Y. Ookubo, T. Morita, Y. Magara, *Water Res.* 32 (1998) 2593–2600.
- [9] N. Hoda, E. Ayranci, in: *Proceedings of the Carbon'03 Conference, Oviedo, Spain, 2003*, p. 225.
- [10] B.E. Conway, E. Ayranci, H. Al-Maznai, *Electrochim. Acta* 47 (2001) 705–718.
- [11] E. Ayranci, B.E. Conway, *J. Appl. Electrochem.* 31 (2001) 257–266.
- [12] E. Ayranci, B.E. Conway, *Anal. Chem.* 73 (2001) 1181–1189.
- [13] E. Ayranci, B.E. Conway, *J. Electroanal. Chem.* 513 (2001) 100–110.
- [14] B.E. Conway, G. Ayranci, E. Ayranci, *Z. Phys. Chem.* 217 (2003) 315–331.
- [15] B.E. Conway, R.G. Barradas, T. Zavidzki, *J. Phys. Chem.* 62 (1958) 676–678.