Thermal Adsorption and Catalytic Photodegradation Studies of Carbendazim Fungicide in Natural Soil and Water

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Abstract

Adsorption characteristics and catalytic photodegradation of carbendazim (methyl benzimidazol-2-ylcarbamate) have been investigated in Kurdistan natural soil and different natural waters (drinking, river, lake and ground water). Physico-chemical properties of the natural soil and water were determined. The equilibrium adsorption of carbendazim onto studied soil samples described by Freundlich adsorption model. The catalytic photodegradation processes were studied in aqueous Titanium dioxide (TiO_2) suspensions under UV radiation. The kinetic study was done by monitoring the concentration during the degradation process, using High performance Liquid Chromatography (HPLC), coupled with UV-visible spectrophotometer. It was found that the photocatalytic degradation process in this work exhibited pseudo first-order kinetics. The rates of catalytic photodegradation of carbendazim in natural water were lower than that in distilled water.

Keywords: Thermal adsorption, Photodegradation, TiO_2 Carbendazim, Fungicide, HPLC, Natural water

1. Introduction

Pesticides are used on a regular basis for agricultural and domestic protection of plants, woods, soils, and to control the growth of certain vegetation. Even though there are many positive features associated with pesticides, some can adversely affect the environment and human health. Many pesticides move from targeted areas to non targeted areas by vitalization and transport to surface water and sediment or by penetration through the soil. Elevated levels of pesticides in water system can render the quality of water unfit for human consumption. The primary transformation processes (hydrolysis, photodegradation, oxidation and biodegradation) are responsible for reducing persistence and diminishing toxicity of pesticides in the environment (Ioannis K. et al., 2001). Many factors govern the potential for ground water or surface water contamination by pesticides. Among these factors: properties of both the soil, and that of the pesticides. Pesticides behave in somewhat predictable ways in the environment. The most important property of pesticides that can be used to predict environmental fate is

adsorption of pesticides on soil (Ronday R. et al., 1996)**.** Carbendazim, is a systemic benzimidazole fungicide, is applied repeatedly to control plant diseases including soil borne diseases, over a growing season (Yunlong Yu et al., 2009) and have been extensively used in Kurdistan to control many types of fungus. It is stale in the environment and undergoes only limited decomposition or degradation under normal ambient condition. (Yarden O.et al., 1985). In soils this compound is retained both by nonionic and ionic sorption processes (Berglof T. et al., 2002). 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 (Aboul-Kass IM T.A.T.and Simoneit B.R.T., 2001). A water treatment based on the chemical oxidation of organic compounds by advanced oxidation processes (AOPs) that is useful for purifying drinking water, natural water and for cleaning industrial wastewater has been used extensively(Grigory Zelmanov and Raphael Semia., 2008).AOPs include photocatalysis systems such as combination of a semiconductor (TiO$_2$, ZnO, etc.) and UV light. TiO$_2$ has been widely used because of its various merits such as low cost, high photocatalytic activity, chemical activity and nontoxicity. However, its applications have been limited for several reasons such as low photon utilization efficiency and need for a high power UV excitation source (V. Mirkhani, S. et al., 2009).The catalytic photodegradation and the kinetics of the degradation processes of pesticides and organic compounds have been investigated in the cases of several types of natural waters and soils(Ioannis K. et al. 2001, Khan M. G. Mostofa et al. 2007). The photolytic behavior of carbindazim fungicide in the presence of TiO$_2$ as a special photocatalyst has been studied by R. Rajeswari and S. Kanmani (R. Rajeswari.et al., 2009) which investigated the optimum condition (40 mgl^{-1}of carbendazim and 1 gl^{-1} of catalyste). The present study deals with the influence of Kurdistan natural water on the rate of carbendazim photodegradation. Furthermore the adsorption characteristics of this fungiside have been studied on Kurdistan soil. This work is continues of the series woks programmed by our group to investigate the effected of Kurdistan nature on the advanced oxidation process and adsorption properties of the pesticides and organic compounds present in Kurdistan.

2. Experimental

2.1 Chemicals

Carbendazim is supplied by Fluka AG with the purity of 98 %. TiO$_2$ (Anatase) used through the present work is supplied by BDH chemicals with the purity 96.85%.Potassium. Acetonitrile and other solvents were HPLC grade and purchased from Tedia Company-USA.

2.2 Sample Collection

2.2.1 Soil samples

The Soil samples selected for this study were collected from Grtjutear 6 Km north Erbil City (north: 36°15'26 east: 43°59'48 elevation: 431m) in April 2010. Fresh soil samples were taken from plough layer (0-15 cm depth). Standard soil characterization methods were followed to provide information on some of the physical and chemical nature of the soils (Kafia M. Shareef and George S et al., 2008) Analysis included the determination of soil organic matter percentage (%SOM), moisture content, loss on ignition, pH and electrical conductivity (Ec) measurement as shown in table 1.

2.2.2 Water samples

River water is taken from Greater-Zab River (45 Km west Erbil City), temperature 29ºC.Lake water is taken from Dwkan Lake (150Km East-Erbil City), temperature 30ºC. Ground water is taken from the well around Erbil City, temperature 29ºC. Drinking water is taken from laboratory tap water. All water samples were collected (in April 2010) in pre-washed polyethylene bottles. pH and electrical conductivity of the samples were measured while collecting the samples. Some physico-chemical properties together with ionic constituent of water samples are shown in table 2 (A & B).

2.3 Analytical methods and instruments

The Electrical conductivity (EC) of the studied soil and water samples was determined by conductivity meter Hi8314. pH was measured by using portable pH–meter (HANNA instrument model PHB) with combined electrode. PerkinElmer series 200 HPLC connected with UV-visible spectrophotometer detector and analytical column (PRT 720041, ET2501814 Nucleosil 120-5 C18 Machereg) was used for determination of residual concentration of carbendazim. The conditions of HPLC process are, Mobile phase: Acetonitrile/Water (70:30 v/v), Flow rate: 0.1 ml/min, Detector wavelength: 254 nm, Injection volume: 20μl, Operating temperature: 30 ºC (Jeong-Heui Choi et al., 2007).The concentration of ions in water determined by Dionex ICS-1000 from USA connected with conductivity detector. The mobile phase for cationic measurement is 20 mM of methanelsulfonic

acid and for anionic measurement are 3.5 mM Na_2CO_3 + 1.0 mM $NaHCO_3$. Bs-11, k109050 water bath-shaker (jeio Teck, korea) used to mixing carbendazim soil solution. 200A Centrifuge from Hermle-Germany (180w, 2060 Nm, 230V) used for separation the carbendazim solution from soil and TiO_2 suspension.

2.4 Equilibrium adsorption procedure

In each adsorption experiment, 10 ml of carbendazim solutions was placed in pre-washed centrifuged tube. Adsorption experiment were conducted with carbendazim initial concentration($C_{\circ}$) 10, 15, 36 and 60 μgml^{-1} the tubes were stirred continuously in a thermostated shaker at 20ºC for 24h contact time. The sample tubes were then centrifuged at 4000 rpm for 30 minutes. The absorbance of the supernatant solution was estimated to determine the residual concentration of carbendazim. The amount of carbendazim adsorbed on the solid was calculated from the difference between its initial concentration ($C_{\circ}$) and its concentration in the solution at equilibrium (C_e).

2.5 Photodegradation procedure

The photodegradation experiments in this study were performed using a laboratory constructed unit.The source of light used is 100-Hg lamp (230V, 50Hz and 1 Am) without selector from Osram- Germany. The lamp was placed at 10 cm apart from the photoreaction cell. The photodegradation experiments were carried out at room temperature (30ºC) in a 35 ml cylindrical photochemical cell. 20 ml of solution (35 $mgml^{-1}$ pesticide and 1 $gl^{-1}$of TiO_2 powder in water samples) was added to the photoreaction cell. The reaction mixture was stirred magnetically in the photoreaction cell and irradiated by a light source. Two milliliters of samples were taken at various irradiation time intervals. The samples were centrifuged to remove the semiconductors and then they were analyzed.

3. Results and discussion

The concentration of carbendazim during the catalytic photodegradation monitored by HPLC through the observing peak intensity retention time 8.15 min (fig. 1).

The intensity of carbendazim peak in HPLC chromatogram decreased gradually indicates the reducing of carbenazim concentration during the photodegradation process. Variation of carbendazim concentration with the time in different of water samples have been shown in fig.2. Data of photodegradation experiments were utilized to fit the pseudo first order rate equation (Jeong-Heui Choi et al., 2010):

$$- \ln \left\{ \frac{[c]}{[c_{\circ}]} \right\} = kt \tag{1}$$

Where [c] is the concentration of carbendazim at time, [$c_{\circ}$] is the initial concentration of pesticides and t, is the exposure time. The graphical method was employed to predict the order of the reaction. The plot of ln [c]/[$c_{\circ}$] versus irradiation time shows straight line behavior as shown in fig.3. This suggests the first-order kinetics of the catalytic photodegradation in the studied water samples.

The reaction rate constants which were determined from the slope of the straight line and the half lives ($t_{1/2}$) which were calculated by equation 2 are tabulated in table 3.

$$t_{1/2}=0.693/k \tag{2}$$

Data in table 2 indicate that the catalytic photodegradation of carbendazim in natural waters was slower than that in distilled water, and were in the following order:

Distilled water>Ground water> Lake water> Drinking water >River water

This may be due to the presence of inorganic ions present in natural water (see tables 2A and 2B) and influence the kinetics and mechanism of the catalytic photodegradation process (Alan M. Shiller et al., 2006). It is well known that the catalytic photodegradation occurs at the surface of the semiconductor particles, so that the specific adsorption of ions may affect the system performance. Specific adsorption of ions can give sacrificial coordination reaction at the oxide-water interface (M. Harir et al., 2008).The surface occupation by anions may compete with the adsorption of organic molecules, this effect being directly related to their coverage fraction. Inhibition by strongly adsorbed anions such as nitrate and perchlorate has been reported by Chantal G. et al. (Chantal Guillard et al., 2005).

Ion chromatographic technique was used to determine the concentration of NO_2^- and NH_4^+ ions liberated during catalytic photodegradation of carbindazim (figs. 4 A & B).

The formation of inorganic ions NO_2^- and NH_4^+ was measured in the course of the irradiation of carbendazim solutions. The changes in concentration of nitrogen containing inorganic ions with the amount of carbendazim remaining at different times of catalytic photodegradation are shown in table 4(A & B).

Increase in amount of NO_2^- and NH_4^+ in all water sampes were observed during the catalytic photodegradation of carbendazim. The NH_4^+ ions were produced at the beginning of the reaction unlike NO_2^- ions which were formed in significant concentrations only after 60 min of degradation process. The increase of the NO_2^- concentration with increasing irradiation time does not involve a decrease of the NH_4^+ ion concentration, thus indicating that the NO_2^- ions are not produced by the oxidation of the NH_4^+ but are produced directly from the intermediate by-products. As previously suggested by Lhomme et al. (Lhomme L. et al., 2005).

For the description of adsorption equilibrium of carbendazim on to the studied soil samples. Freundlich equation was used in the folowing form (Febrianto J. et al., 2009):

$$Log \ q_e \ = \ Log \ K_F + \ n \ Log \ C_e \qquad\qquad (3)$$

Where q_e is the amount of carbendazim adsorbed (μgg^{-1}), n is adsorption intensity, C_e is the concentration of carbendazim (μgml^{-1}) at equilibrium and K_F is the Freundlich adsorption coefficient (mlg^{-1}). FIG. 5 represente the plot of Log q_e versus Log C_e (fig.5) for adsorption of carbendazim on the studied soil samples. Values of K_F, n and correlation coefficient (R^2) for adsorption of carbendazim were summarized in Table 5. The values of correlation coefficient ($R^2 > 0.94$) together with the linear plot in fig. 5 confirm the validity of Freundlich model to describe the adsorption equilibrium of carbendazim onto the studied soil samples. Values of n the adsorption isotherm is lower than unity for studied soil. The parameter n is a linearity factor its a measure of the extent of the heterogeneity of sorption sites having different affinities for solute retention by matrix surfaces, where sorption by the highest energy sites takes place preferentially at the lowest solution concentrations (Stearman G.et al.,1989).

The K_F values were between 4.62 and 8.10 at temperature range $20 – 40^{\circ}C$. The results indicate that the highest values of K_F in general, and at all temperatures, corresponded to soils with the high clay and organic matter contents. This is because the adsorption capacity of soil for organic pollutants is due to its organic carbon content (Boyed, S.A. et al.,1988). Results obtained in the present study were similar to those reported by Zheng and Obbard (Zheng, Z., and Obbard, J. P., 2002), Muherei (Muherei, M.A., 2009), Rodriguez (Rodriguez, 2005). Data in table 5 revealed that value of K_F increased as the temperature raised. The increase in carbendazim uptake with increasing temperature may be due to either higher affinity of sites for carbendazim or an increase in the number of binding sited on the soil (Marques, A.M. et al.1991). Moreover the change in K_F value with temperature may be due to the salvation of carbendazim molecules. The degree of salvation is essentially different at each temperature, because the carbendazim – solvent interactions are very sensitive to temperature. Increasing temperature gradually desolvates the head group, making it less hydrophilic and more compact, and this increases surface activity and saturation adsorption values.

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Table 1. Some Physico-chemical properties of selected soil samples

Physico-chemical properties	Values
SOM%	1.1
Moisture %	2.26
Loss on Ignition %	4.39
pH in Distilled water	7.75
Ec(mSm^{-1})	66.4

Table 2A. pH, EC and concentration of anions in water samples

Water Sample	pH	EC μscm-1	NO_3^- mgl^{-1}	SO_4^{-2} mgl^{-1}	PO_4^{-3} mgl^{-1}	Cl^- mgl^{-1}	F^- mgl^{-1}
Distilled Water	7.14	12	N.D	0.01	N.D	0.014	N.D
Ground Water	7.42	280	7.327	2.984	4.986	3.456	0.020
Lake Water	7.65	290	8.93	28	6.3	4.65	0.026
River Water	7.69	315	11.46	43	5.8	2.86	0.028
Drinking Water	7.82	328	6.94	16	5.54	8.00	0.019

Table 2B. Concentration of cations in water samples

Water Sample	Na^+ mgl^{-1}	K^+ mgl^{-1}	NH_4^+ mgl^{-1}	Mg^{+2} mgl^{-1}	Ca^{+2} mgl^{-1}
Distilled Water	N.D	N.D	N.D	N.D	0.035
Ground Water	12.906	8.312	0.048	18.23	30.30
Lake Water	11.6	7.16	0.069	17.01	26.8
River Water	10.3	7.29	0.057	14.4	28.2
Drinking Water	11.01	7.13	0.05	17.5	30.1

Table 3. Kinetic parameters of carbendazim photodegradation in different water samples

Water Sample	K(min^{-1})	$t_{1/2}$ (min)
Distilled Water	0.0394	17.588
Ground Water	0.0388	17.860
Water Lake	0.0357	19.411
River Water	0.0303	22.671
Drinking Water	0.0323	21.4551

Table 4A. Concentration of NO_2^-, NH_4^+ and carbendazim during the catalytic photodegradation in distilled, ground and lake water

t(min)	Distilled Water			Ground Water			Lake Water		
	Carbendazim mgl^{-1}	NH_4^+ mgl^{-1}	NO_2^- mgl^{-1}	Carbendazim mgl^{-1}	NH_4^+ mgl^{-1}	NO_2^- mgl^{-1}	Carbendazim mgl^{-1}	NH_4^+ mgl^{-1}	NO_2^- mgl^{-1}
0	35	0	0	35	0.048	7.327	35	0.069	9.93
30	16.51	0.25	0.00	18.17	0.301	7.372	24.04	0.361	9.90
60	6.36	1.6	0.2	7.82	1.712	7.55	14.66	1.701	10.1
90	3.16	4.9	0.84	4.89	5.06	8.41	8.06	.5.1	10.74
120	0	6.3	1.9	0	6.37	9.37	3.22	6.4	12.4

Table 4B. Concentration of NO_2^-, NH_4^+ and carbendazim during the catalytic photodegradation in river and drinking water

t(min)	River Water			Drinking Water		
	Carbendazim mgl^{-1}	NH_4^+ mgl^{-1}	NO_2^- mgl^{-1}	Carbendazim mgl^{-1}	NH_4^+ mgl^{-1}	NO_2 mgl^{-1}
0	35	0.057	11.48	35	0.053	6.44
30	21.6	0.261	11.53	25.2	0.273	6.49
60	9.68	1.59	11.78	14.93	1.49	6.74
90	7.16	5.02	11.84	10.75	5.3	7.57
120	0	6.48	13.63	4.1	6.41	9.40

Table 5. Equilibrium adsorption parameters

Temperature	$K_{F\ ml.g}^{-1}$	n	R^2
$T_1=20^\circ C$	4.62	0.51	0.94
$T_2=30^\circ C$	6.03	0.53	0.95
$T_3=40^\circ C$	8.100	0.52	0.96
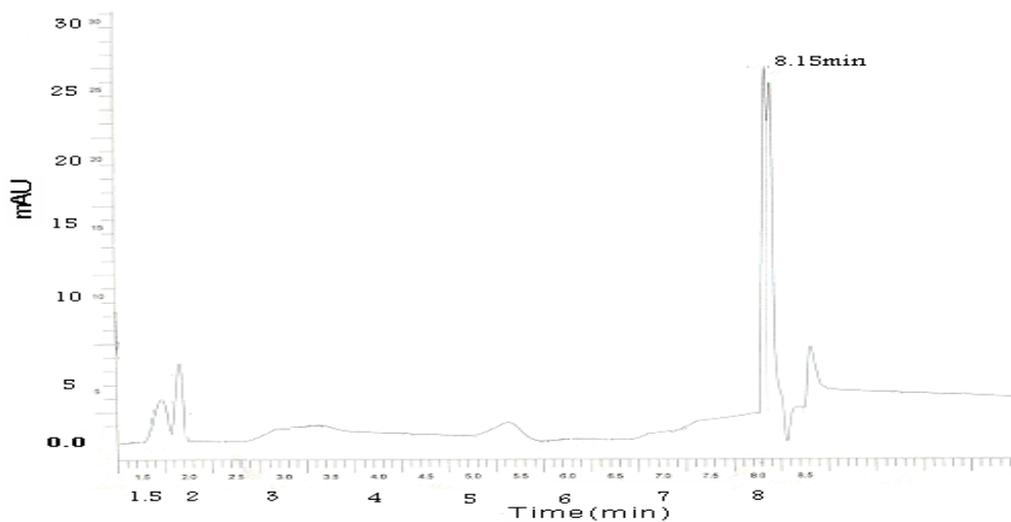
Figure 1. HPLC Chromatogram of 35 mgl^{-1} Carbendazim before degradation
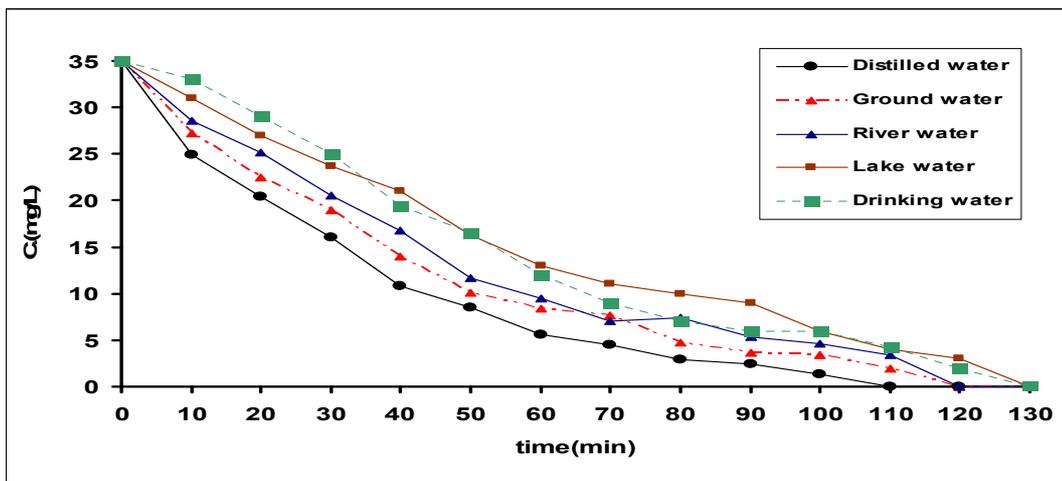
Figure 2. Catalytic photodegradation of 35 mgl^{-1}, carbendazim over 1 gl^{-1} TiO$_2$, in different types of water

$$y = -0.0303x$$
$$R^2 = 0.903$$
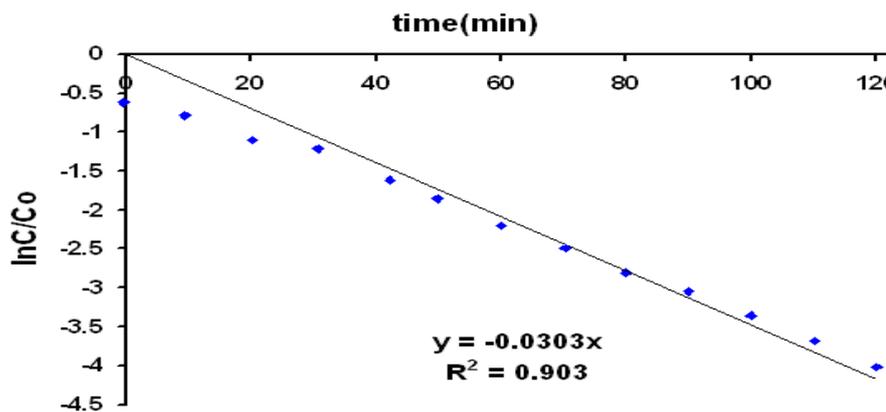
Figure 3. Plott of ln(C/C$_o$) versus t of catalytic photodegradation in Lake Water

$1 = F^-$
$2 = Cl^-$
$3 = NO_2^-$
$4 = SO_4^{-2}$
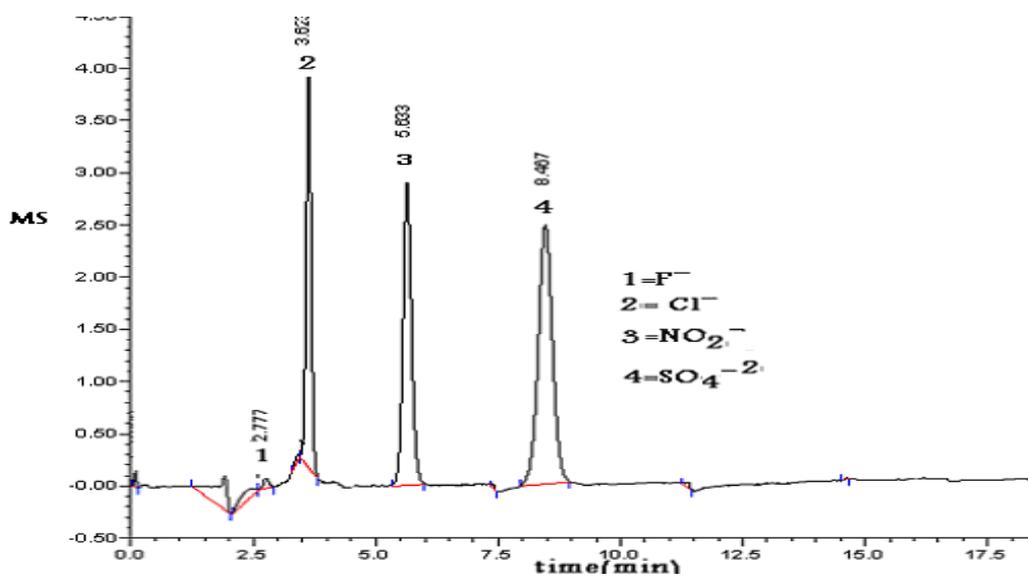
Figure 4A. Anionic IC Chromatogram of carbendazim in ground water before photodegradation
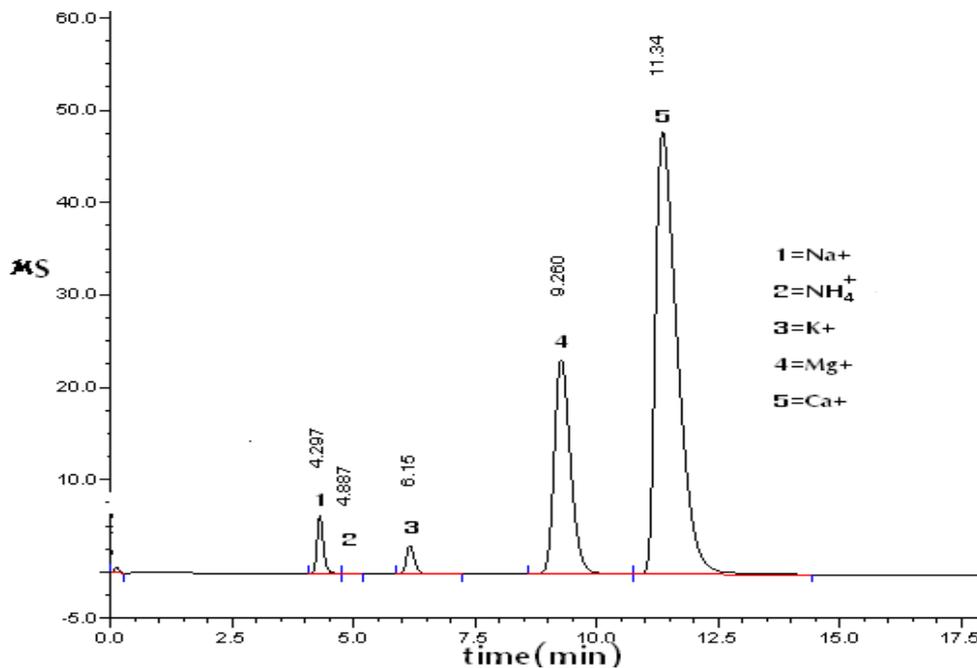
Figure 4B. Cationic IC Chromatogram of carbendazim in ground water before photodegradation
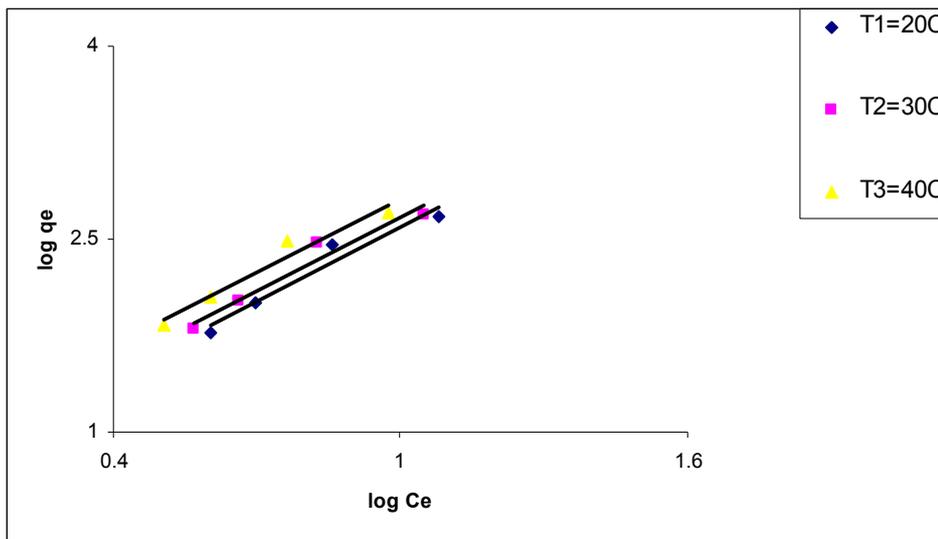
Figure 5. Freundlich isotherm Parameters for carbendazim adsorption on the studied soil at different temperatures