



Adsorption-desorption behaviour of chlorimuron-ethyl herbicide on homoionic clays

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Abstract

Laboratory studies were conducted to determine the adsorption-desorption behaviour of Chlorimuron-ethyl herbicide on three homoionic clays (Kaolinite (K), Mica (M) and Bentonite (B)), which are found in Indian soils. The adsorption-desorption data of chlorimuron-ethyl fitted well to Freundlich adsorption-desorption isotherm model ($R^2 = 0.755$ to 0.986). The computed value of $\log K$ and $1/n$ varied from 4.0199 (B-Cu) to 4.1144 (B-Ca) and from 0.4458 (M-Cu) to 0.7894 (K-Ca) respectively. Desorption data of chlorimuron-ethyl were also fitted to Freundlich model and the values of $\log K'$ and $1/n'$ ranged from 4.2727 (K-Ca) to 4.2933 (M-Ca) and from 0.0006 (B-Cu) to 0.0033 (B-Ca), respectively. Higher values of desorption index n'/n indicated poor reversibility of chlorimuron ethyl by soil clays.

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Introduction

The fate of the pesticides in the environment is governed by adsorption-desorption, volatilization, leaching, chemical and biological degradation, preferential flow and runoff processes. All these processes are interdependent upon each other (Khan 1980; Schnoor 1992). Adsorption-desorption processes of chemicals influence their transport and consequently affect their bioavailability. The factors governing pesticide sorption include soil organic matter, the nature and content of the clay, soil water content, soil pH and the chemical structure of the pesticide (Dragun 1998). The pesticide sorption process incorporates a wide range of different chemical mechanisms including ion exchange, cation-bridging, ion-dipole interactions, ligand exchange, charge transfer, hydrogen bonding and van der Waals' forces (Bailey and White 1970; Sposito 1984).

Chlorimuron-ethyl (ethyl 2-[[[(4-chloro-6-methoxypyrimidin-2-yl) amino] carbonyl] amino] sulfonyl] benzoate), trade name classic is a member of sulfonylurea group of herbicides specifically applied on soybean fields to control weeds before or after their germination (Reddy et al. 1995). The herbicide inhibits acetolactate synthase (ALS), an important enzyme necessary for biosynthesis of branched-chain amino acids isoleucine, leucine, and valine with both soil and foliar activity (Vencilli, 2002). Residual chlorimuron-ethyl herbicide can remain intact in the soil for many months and may cause toxicity to herbicide sensitive crops

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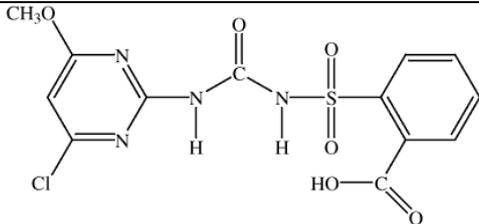
in the rotation such as maize, sorghum, canola, melon, potato, and sugar beet, thereby reducing the maximal usefulness of these chemicals (Soltani et al., 2006). Several studies pertaining to the adsorption-desorption behavior of the herbicide in different soils have been reported in the literature (Wang et al., 2007) but no information is available on the adsorption-desorption behavior of Chlorimuronethyl in different types of clays which form an important part of soil matrix. The present study was undertaken to investigate the concentration dependent adsorption-desorption of the herbicide on homoionic saturated clays.

Material and Methods

Herbicides and Chemicals

Chlorimuron-ethyl of 92.0% purity grade was obtained from Reposo SAIC, Argentina. The chemical structure and the main physicochemical properties of chlorimuron ethyl are shown in Table 1 (Roberts 1998). Chemicals and solvents used in the study were of HPLC grade and procured from E. Merck, India.

Table 1. Chemical Structure and some physico-chemical properties of Chlorimuron ethyl

Chemical structure	
Molecular Formula	C ₁₅ H ₁₅ ClN ₄ O ₆ S
Molecular Weight	414.821 amu
Color/Form	Crystals from butyl chloride White solid, Colorless crystals
Melting Point	181°C
Density/Specific Gravity	1.51 at 25°C
Dissociation Constants	pKa = 4.20
Octanol/Water Partition Coefficient	log K _{ow} = 2.50
Solubilities	Low solubility in organic solvents
Vapour Pressure	4.0X10 ⁻¹² mm Hg at 25° C
Toxicity	(Rat): Oral LD ₅₀ > 4000 mg/kg. (Rabbit): Dermal LD ₅₀ > 2000 mg/kg
Sensitive Weeds	Common ragweed, redroot pigweed, and velvetleaf
Application Methods	Postemergence
Residual Activity	Chlorimuron will provide some limited residual activity after application.
Unique Characteristics	A non-ionic surfactant must be added at 0.2% v/v. 28% Urea ammonium nitrate (U.A.N.) at 2 L/ha will improve the control of velvetleaf. Typical symptoms of plant death (chlorosis, necrosis) may occur from 1-3 weeks after application, depending on growing conditions. Favorable growing conditions will speed the activity while cool or dry conditions will delay activity

Clay Characterization

Samples of aluminosilicate clays namely, kaolinite, bentonite and illite were obtained from Department of Soil Science, G.B. Pant University of Agriculture and Technology, Pantnagar, India. Purified clays (7g each) were taken in six centrifuge tubes for preparation of homoionic (Ca⁺² and Cu⁺²) saturation. Three centrifuge tubes containing each type of clay were treated with 20 mL of 0.1M CaCl₂ and the other three tubes were treated with 20 mL of 0.1M CuCl₂ solution. The tubes were equilibrated on a horizontal shaker and allowed to stand for 30 minutes. They were then centrifuged at 8000 rpm for 15 minutes and then the supernatant was removed. The process was repeated five times till the clays become saturated with metal ions. In order to remove entrapped electrolyte, clays were repeatedly washed with 20 mL of 60% methanol and centrifuged till the supernatant test was negative for the chloride ions.

The cation exchange capacity (CEC) of clays was determined by Ba^{+2} - Mg^{+2} exchange on Ba^{+2} saturated clays prepared by the procedure described above (Gillman and Sumpter, 1986). Specific surface area of the clays was determined by ethylene glycol method (Bower and Goertzen, 1952).

The XRD patterns ($5\text{-}120^\circ 2\theta$) of Ca^{+2} - bentonite, -kaolinite and -mica were obtained by using a Praker-AXS diffractometer equipped with Cu-anticathode and graphite monochromator following the procedure outlined by Tan (1996).

The XRD patterns of Ca^{+2} saturated minerals (Figure 1) revealed that bentonite sample was not pure and a peak at 4.494 \AA indicated the presence of vermiculite, muscovite and illite along with montmorillonite. The peaks at 4.26 , 3.349 , 3.242 , 2.458 and 1.542 \AA revealed the presence of dickite, quartz, K-feldspar, olivine in bentonite sample, respectively. A peak at 1.542 \AA indicated the presence of biotite and trioctahedral chlorite in the bentonite sample. The XRD pattern of Ca^{+2} -kaolinite showed the characteristic peaks of kaolinite at 7.202 , 4.458 and 1.488 \AA besides the presence of quartz, bayerite, ilmenite, and boehmite. The XRD pattern of Ca^{+2} - mica showed the characteristic peak of mica at 9.955 \AA besides the presence of illite, muscovite, illite and gypsum.

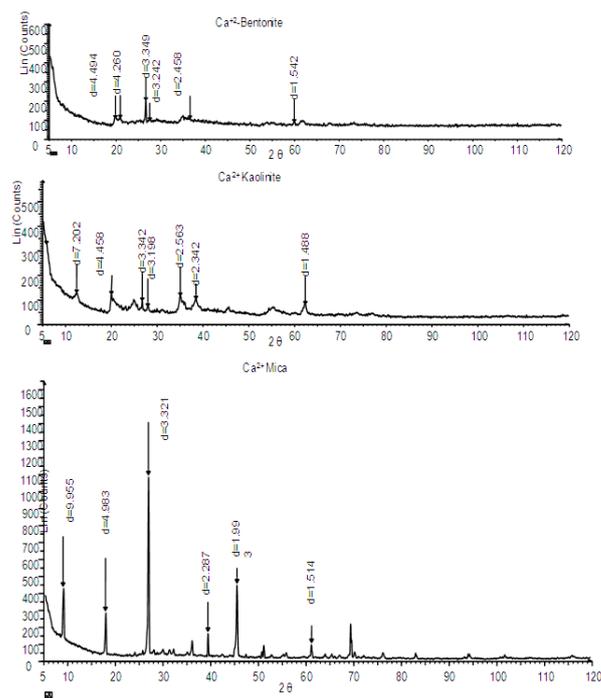


Figure 1. X-ray diffraction patterns of Ca^{+2} -clay samples

Adsorption experiments

Twenty milligrams of all homoionic clays were taken in centrifuge tubes. In three of them 2 mL of 0.1M CaCl_2 solution was added whereas in other three 2mL of 0.1M CuCl_2 was added. The volume in each tube was made to 19 mL by addition of double distilled water. The samples were kept for 24 h, and thereafter 1mL of chlorimuron-ethyl of different conc. (2, 5, 10, 15 and 20 mg L^{-1}) was added to it. The mixtures were shaken in duplicate for 24 h, centrifuged (7000 rpm) and supernatants were stored in glass vials.

Desorption experiment

Homoionic clays (20 mg each clay) which were equilibrated with 1 mL of 20 mg L^{-1} chlorimuron-ethyl in adsorption study were used for desorption study after the centrifugation (7000 rpm) and separation of supernatants. Homoionic clay pellets in duplicate were equilibrated with 20mL of 0.01M CaCl_2 or CuCl_2 as per the case. The reaction mixtures were kept on an orbital shaker at 150 rpm for 24 h at room temperature (28°C). After equilibration, the mixtures were centrifuged and the supernatants were stored in glass vials. The process was repeated several times till chlorimuron-ethyl residues were not detected in the supernatant.

Extraction of Chlorimuron-ethyl

The supernatants of kinetic, adsorption and desorption studies were transferred to separating funnels and extracted twice with dichloromethane (DCM) solvent. The pooled DCM layer was collected and passed through a column of anhydrous sodium sulphate to remove the moisture content and thereafter, evaporated to dryness on a flash evaporator at 40°C . The residue was dissolved in HPLC grade methanol and filtered through $0.45\mu\text{m}$ Millipore filter prior to HPLC analysis.

HPLC Analysis

Herbicide concentrations were determined by using a HPLC system (Dionex Ultimate 3000, Dionex India Pvt. Ltd.), equipped with a quaternary pump, a variable wavelength UV-VIS detector, RP-18 (250 mm x 4.6mm i.d., particle size 120\AA) column. The mobile phase was a 70/30(v/v) mixture of HPLC grade Methanol /Triple Distilled Water /0.1% (v/v/v) glacial acetic acid. Flow rate of the mobile phase was at 1.0mL/min. Chlorimuron-ethyl samples were detected at 256 nm at room temperature (25°C). The retention time of Chlorimuron-ethyl was 4.38 min under the above conditions. Data were collected and processed using computing integrator chromatography workstation (Chromeleon software).

Results and Discussion

Some investigated properties like size, shape, surface area and cation exchange capacity of three different clays namely kaolinite, bentonite and illite are presented in Table 2.

Table 2. Clay characterization/properties

Properties	Bentonite	Kaolinite	Illite
Size (μm)	0.01-1.0	0.5-5.0	1-2
Shape	Flakes	Hexagonal	Dioctahedral
Surface area (m^2/g)	259.35	2.58	35.16
Cation Exchange Capacity ($\text{cmol}(\text{p}^+) \text{kg}^{-1}\text{unit}$)	70.0	8.0	8.5

The data on the percent recovery of Chlorimuron ethyl from calcium and copper saturated clays at two different concentrations are depicted in Table 3. It is evident from the data that the percent recovery of chlorimuron ethyl from all the three metal saturated clays was higher at 20 mg L^{-1} concentration than at 10 mg L^{-1} . Among the homoionic clays, the highest recovery was found in kaolinite- Cu^{+2} and the lowest in mica- Cu^{+2} at both the concentrations which could be related to the variation in the adsorbed amounts of chlorimuron-ethyl by the homoionic clays.

Table 3: Percentage recovery (%) of Chlorimuron-ethyl

Clays	10 mg L^{-1}	20 mg L^{-1}
K-Ca	72.29	97.91
M-Ca	85.42	91.47
B-Ca	80.69	85.64
K-Cu	88.86	98.96
M-Cu	70.49	78.76
B-Cu	82.28	95.55

Adsorption Studies

Adsorption of chlorimuron-ethyl on three clays revealed that adsorption increased with the increasing amount of the herbicide (Figure 2).

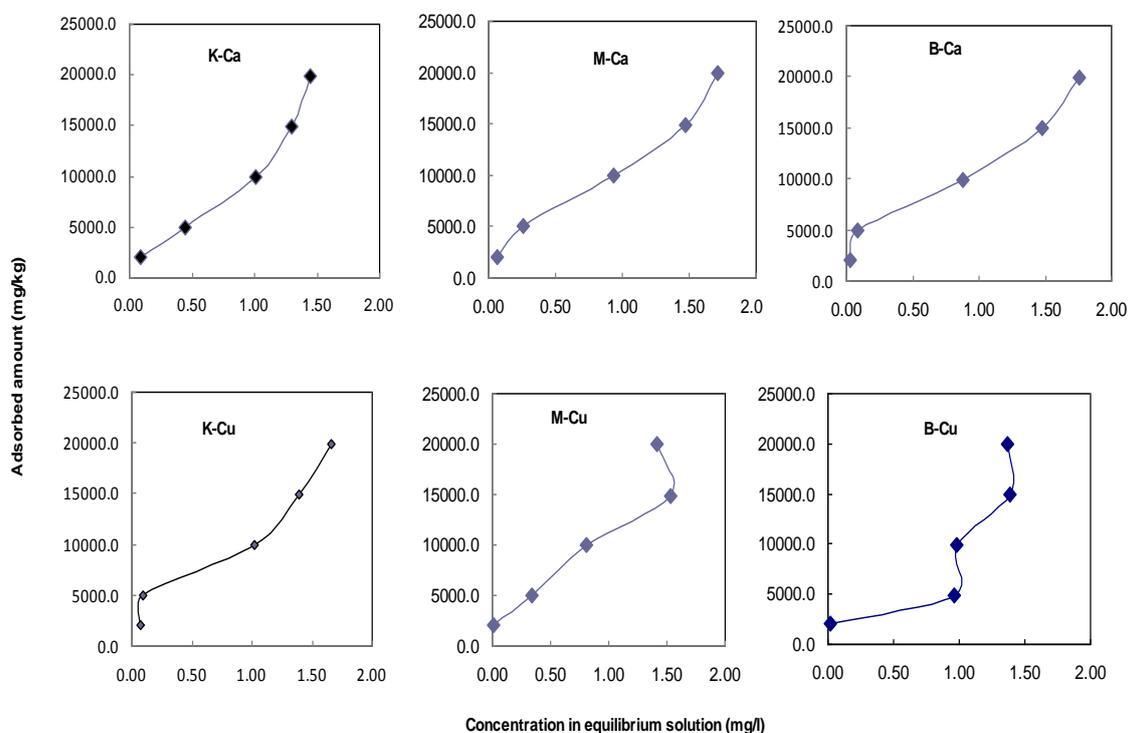


Figure 2. Adsorption isotherms of chloromuron ethyl on different homoionic clays.

In general, beyond 1 mg L⁻¹ equilibrium concentration of chlorimuron-ethyl the rate of increase in adsorption was relatively higher than at lower concentration, indicating thereby the possible formation of multimolecular layer on the surface of the adsorbent. Among clays, higher adsorption was recorded with kaolinite, a 1:1 mineral as compared to mica and bentonite. High adsorption of chlorimuron-ethyl on kaolinite as compared to mica and bentonite could be due to anionic behavior of this herbicide which has a pKa value of 4.2. This behavior allows the anionic species to be readily attracted by the positively charged sites present on the broken edges of 1:1 type clays. [Ukrainczyk and Ajwa \(1996\)](#) also proposed hydrophobically driven adsorption, dipole-dipole interactions, and anion exchange by outer sphere complex formation on pH dependent charge sites as three possible mechanisms of adsorption of primisulfuron, a sulfonylurea on minerals and soils. The type and amount of clay could affect adsorption due to surface area and surface charge ([Obrigawitch et al., 1981](#)). Adsorption study carried out with five sulfonylurea herbicides (bensulfuron-methyl, chlorimuron-ethyl, nicosulfuron, monosulfuron and metsulfuron-methyl) on four typical sorbents including montmorillonite, kaolin, diatomite and humic acid also revealed that diatomite had lowest affinity for tested herbicides, kaolin had highest affinity for bensulfuron-methyl, chlorimuron-ethyl and nicosulfuron while montmorillonite and HA had highest affinity for monosulfuron and metsulfuron-methyl, respectively (<http://www.technology articles.org>).

The adsorption data were fitted to Freundlich adsorption isotherm model (Figure 3) and the values of Freundlich constants and R² are presented in Table 4. The values of R² varied from 0.755 to 0.986 which were statistically significant at p=0.05. This indicated that the adsorption data of Chlorimuron-ethyl conformed well to Freundlich adsorption model. Wang et al. 2007, also reported that the processes of adsorption and desorption for chlorimuron-ethyl in soil are nonlinear, and the curves of the isotherm adsorption coincide with the Freundlich model. In most of the cases the adsorption isotherms for clay-pesticide interaction have been found to follow Freundlich adsorption isotherm and are either S- or L-shaped ([Singhal and Singh, 1978](#); [Yaron and Saltzman, 1972](#); [Garg and Agnihotri, 1984](#); [Basham et al., 1987](#)). The values of log K varied from 4.0199 to 4.1144. In general, Cu⁺² saturation increased the values of log K for both kaolinite and mica but log K value recorded for Ca⁺² saturated bentonite was higher as compared to Cu⁺² saturated bentonite clay. Higher log K values for Ca⁺² saturated bentonite could be attributed to the fact that the presence of Ca⁺² as saturating cation ensures relatively more open structure of this expendable mineral. Significant penetration of cinosulfuron in the interlayers of montmorillonite had been reported by [Pantani et al. \(1994\)](#).

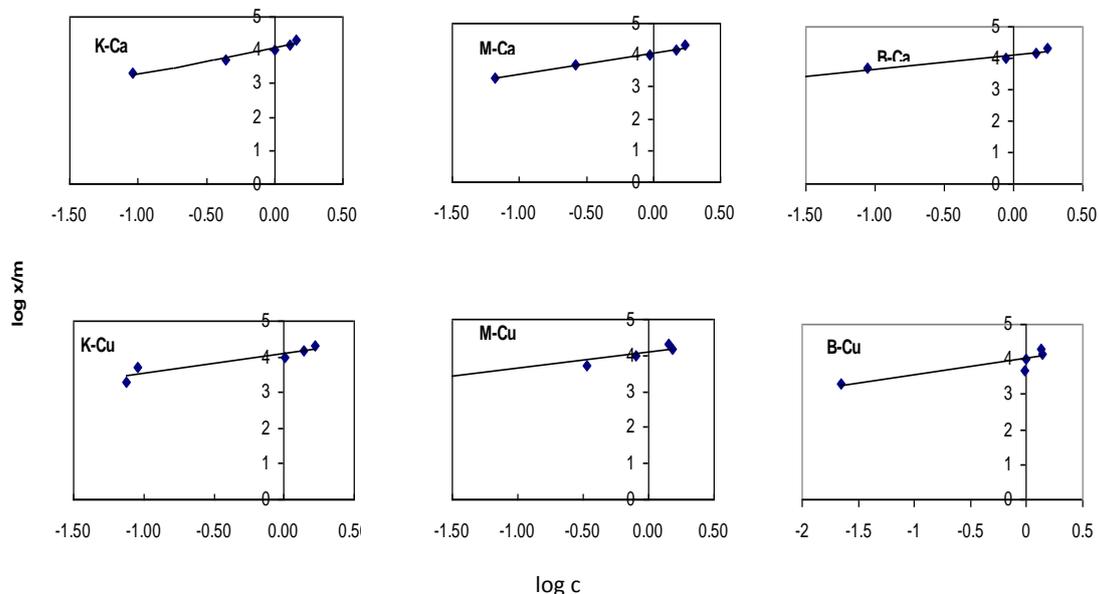


Figure 3. Freundlich adsorption isotherms of chlorimuron ethyl on different homoionic clays.

The values of $1/n$ varied from 0.4458 to 0.7894 which signified higher affinity of chlorimuron ethyl for adsorption sites. Among clays, kaolinite had higher values of $1/n$ as compared to mica and bentonite. Further $1/n$ values for Ca⁺² saturated clays were higher than those of Cu⁺² saturated clays. A lower value of $1/n$ indicated the involvement of sites of relatively lower bonding energy adsorption process.

Table 4. Freundlich adsorption ($\log K$ and $1/n$), desorption ($\log K'$ and $1/n'$) parameters and desorption index (n'/n) of Chlorimuron-ethyl

Clays	$1/n$	$\log K$	R^2	$1/n'$	$\log K'$	R^2	Desorption index
K-Ca	0.789	4.070	0.958	0.0029	4.273	0.985*	272.2
M-Ca	0.665	4.079	0.986	0.0018	4.293	0.424	369.4
B-Ca	0.475	4.114	0.965	0.0033	4.287	0.643	143.8
K-Cu	0.563	4.097	0.875	0.0009	4.273	0.552	625.6
M-Cu	0.446	4.083	0.909	0.0009	4.278	0.464	495.3
B-Cu	0.453	4.020	0.755	0.0006	4.279	0.498	754.3

Desorption studies

The desorption data also fitted well to Freundlich desorption isotherms model (Figure 4) and the computed values of desorption capacity ($\log K'$), order of desorption ($1/n'$), coefficient of determination (R^2) and desorption index (n'/n) are shown in Table 4. The computed values of coefficients of determination (R^2) varied from 0.424 to 0.985 and most values were statistically not significant due to lower number of point in most of the cases. The values of $\log K'$ varied from 4.2727 (K-Ca) to 4.2933 (M-Ca). The values of $1/n'$ ranged from 0.0006 to 0.0033. As compared to adsorption isotherm slope ($1/n$) the desorption isotherm slopes ($1/n'$) were lower indicating hysteretic desorption behavior of clay minerals for chlorimuron ethyl. Similar desorption behavior had been reported in respect of other sulfonylurea herbicides like metasulfuron-methyl (Berglof et al., 2003) and triasulfuron (Pusino et al., 2003). In general, the values of $1/n'$ were relatively lower with Cu^{+2} as saturating cation as compared to Ca^{+2} . The values of desorption index (n'/n) varied from 143.79 (B-Ca) to 754.33 (B-Cu). In general, higher values of desorption index indicated poor reversibility of adsorbed chlorimuron-ethyl. Interestingly, the lowest value of n'/n was noted in the case of (B-Ca) which kept the bentonite lattice in expandable state allowing free access of the molecules while the highest values of n'/n was recorded with B-Cu which could irreversibly retain chlorimuron-ethyl possibly due to formation of its stable complexes with Cu^{+2} on the exchange sites. Pantani et al. (1994) also noted that cinosulfuron adsorbed on Na-, Ca- and Al-montmorillonite was almost completely removed by water washings, whereas on Cu-montmorillonite about half of the adsorbed amount remained bound.

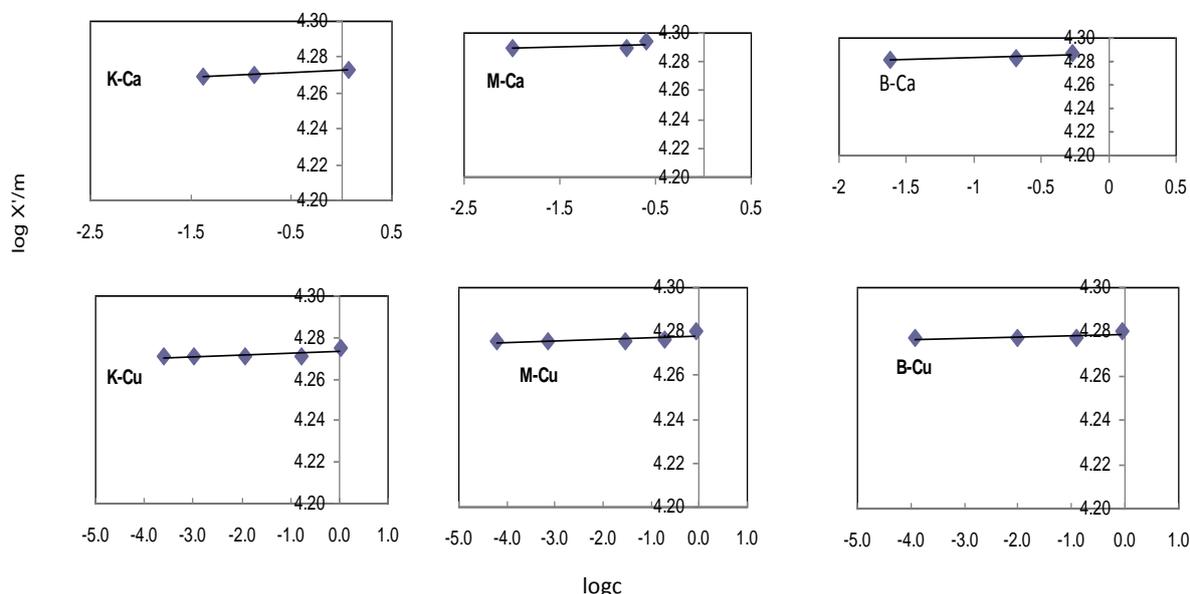


Figure 4. Desorption isotherms of chlorimuron ethyl on different homoionic clays.

Thus, adsorption-desorption of chlorimuron ethyl on homoionic kaolinite, bentonite and mica conform to Freundlich isotherm model. Among clays, the highest adsorption was on kaolinite due to retention of anionic species onto positively charged broken edges of kaolinite. As regards the effect of saturating cation on adsorption, Cu^{+2} saturated kaolinite and mica had higher $\log K$ and $1/n$ values than those with Ca^{+2} saturation due to higher polarisability of Cu^{+2} while Ca^{+2} saturated bentonite had higher $\log K$ but lower $1/n$ than Cu^{+2} saturation due to possible intercalation allowing higher desorption under Ca^{+2} saturation. High desorption index (>100) indicated a higher degree of non-reversibility of adsorbed chlorimuron ethyl with little potential danger of ground water pollution and the effect was more pronounced under Cu^{+2} saturation.

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