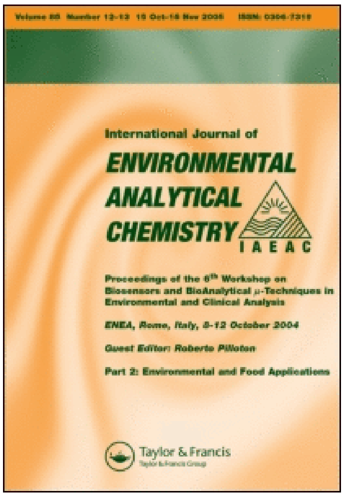

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Effect of ionic strength and pH on the adsorption of selected herbicides on Amberlite

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The effect of ionic strength on the adsorption of alachlor, trifluralin, and prometryn on Amberlite XAD-4 polymeric resin is studied. Static adsorption experiments are carried out at pH 3–6.5 and ionic strength 0.01–2 M at 20°C. By increasing the ionic strength, the adsorption of herbicides can be significantly increased. The electrolyte addition affects both the effectiveness and efficiency of adsorption, leading eventually to a saturation of the resin surface. An explanation of the alteration of adsorption mechanisms, caused by ionic strength, is given, based mainly on the reduction in repulsive forces at the resin–herbicide interface and between adsorbing herbicide molecules, since both resin and herbicides have a polar ring as part of their structure.

Keywords: Adsorption; Polymeric resins; Pesticides; Ionic strength; Chromatography

1. Introduction

Adsorption is a method for the removal of herbicides from water, since these substances are toxic, causing environmental problems through contamination of aqueous systems and grounds. So far, adsorption of pesticides on resins has been studied [1–9]. The capability of an adsorbent to adsorb organic molecules is determined by its nature and physical characteristics (porosity, surface area, etc.) as well as the adsorbate chemical structure and environmental conditions (pH, ionic strength, temperature, additives).

Ionic strength is one of the major factors affecting adsorption. The presence of neutral electrolytes in aqueous solution containing an organic adsorbate is expected to influence the solvent power as well as the interactions between solvent–solute and solute-adsorbent molecules. The cumulative result in adsorption caused by any change in ionic strength of a solution will be determined by the relative magnitude

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of the changes in interactions involved in a particular system. Therefore, adsorption could be increased or decreased [10].

In the present work, the effect of ionic strength on herbicide adsorption upon XAD-4 resin by adding sodium chloride in aqueous solution was examined. The selection of herbicides was based on their different chemical structure, namely their hydrophobicity/hydrophilicity ratio, type of substituents, molecular weight, and solubility in water, in combination with their use in agricultural field. Static adsorption experiments were performed with alachlor, prometryn, and trifluralin [11, 12] at 20°C and at pH 3 and 6.5. The ionic strength was in the range of 0.01–2 M. The effect of ionic strength was related to the resin structure, solute composition and structure, and solution pH.

2. Experimental

2.1 *Materials*

The resin XAD-4 [13] is a rigid, non-ionic, cross-linked macroreticular copolymer of styrene and divinylbenzene, with a high surface area and aromatic nature at its surface. Amberlite XAD-4, supplied from Rohm & Haas Company (Philadelphia, PA), is a polymeric adsorbent with excellent physical, chemical, and thermal stability, and it is also stable at all pH ranges in aqueous solution. Its characteristic pore-size distribution makes this Amberlite an excellent adsorbent of organic substances of relatively low molecular weight [13]. The physical properties of the resin are: porosity (mL pore/mL bead dry basis) 0.35–0.50, surface area ($m^2 g^{-1}$ dry basis) 750, average pore diameter (Å dry basis) 50 and mean particle size (mesh) 40.

Alachlor was supplied by Monsanto (technical grade, purity 95%), whereas both prometryn and trifluralin were supplied by Makhteshim–Agan (analytical grade, purity 99.5%). The chemical structure of herbicides and their main physical properties are given in table 1 [11].

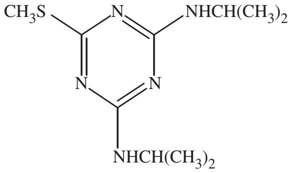
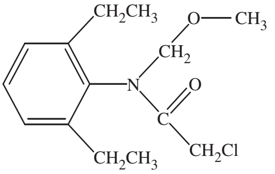
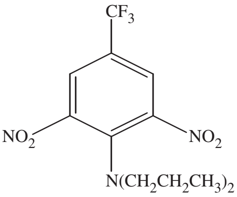
2.2 *Purification of resin*

The beads of the examined resin (Amberlite XAD-4) were cleaned by extraction using methanol as a solvent, for the removal of the residual monomer, remaining trapped within the pore structure after polymerization. This monomer has a wide-band ultraviolet absorbance, which interferes with the spectrophotometric determination of herbicides. In particular, 100 g of beads was extracted three times with 200 mL of methanol for 2 h each time, and they were then washed five times thoroughly with 200 mL of distilled water each time to displace any residual methanol and washed four times with 200 mL of a solution of selected pH and ionic strength each time.

2.3 *Preparation of herbicides solutions*

Herbicides were primarily dissolved in methanol (1000 mg L^{-1}) to accelerate their dissolution in water. Using these initial methanolic solutions, a number of solutions of buffered pH (3 and 6.5) and ionic strength 0.01 were prepared, by dissolving known quantities of analytically pure reagents in distilled and deionized water in proportions specified by Perrin [14]. The adjustment of ionic strength in the range

Table 1. Herbicide structures and properties [11].

Herbicide structure/ properties	Prometryn	Alachlor	Trifluralin
Chemical structure			
Molecular form	$C_{10}H_{19}N_5S$	$C_{14}H_{20}ClNO_2$	$C_{13}H_{16}F_3N_3O_4$
Appearance	White powder	Yellow–white to wine red, odourless solid	Yellow–orange crystals
Solubility in water (20–25°C)	$33\,mg\,L^{-1}$ (25°C)	$242\,mg\,L^{-1}$ (25°C)	$0.184\,mg\,L^{-1}$ (pH 5) $0.221\,mg\,L^{-1}$ (pH 7) (25°C)
Density ($g\,cm^{-3}$)	1.150 (20°C)	1.125 (25°C)	1.360 (22°C)
p*K*a (21°C)	4.1	–	–
K_{ow}^{a}	$\log P = 3.1$ (unionized)	$\log P = 3.09$	$\log P = 4.83$ (20°C)
Mol.wt.	241.4	269.8	335.3
Melting point (°C)	118–120	40.5–41.5	48.5–49

[a] K_{ow}: Partition coefficient between *n*-octanol and water (as a log value).

of 1–2 M was achieved by adding the appropriate quantity of sodium chloride in herbicide aqueous solutions. The used initial concentration of the solutions of each herbicide was in the range $200–1000\,mg\,L^{-1}$.

2.4 *Equilibrium adsorption experiments*

Experimental equilibrium adsorption data were obtained by static adsorption experiments at 20°C as follows. The wet beads (approximately 0.5–1 g dry weight) were weighed and shaken with 10 mL of known initial concentration buffer solution of herbicide (C_o). It should be noted that since the wet beads were kept active in each buffer solution, their addition caused dilution of the initial solution. Then, the conical flasks which contained the aqueous solutions, were completely sealed and shaken in a shaking water bath (Unitronic 320 OR model, Selecta P) at a pre-determined temperature at 60 rpm until equilibrium was reached. Continuous sampling showed that approximately 4 h of shaking was required for equilibrium to be obtained [15]. The equilibrium herbicide concentration (C_{eq}) in the solution was determined from the aqueous phase analysis by HPLC with the following characteristics: GBC LC 1120 pump and GBC 1200 UV/VIS detector (GBC Scientific Equipment Pty Ltd, Australia), JCL 6000 software (Jones Chromatography Ltd, USA) and reversed-phase column: 250 × 4.6 mm, Hypersil C18 BDS with a particle size of 5 µm. The conditions for the analysis of herbicides are given in table 2. The amount of retained herbicide on the resin was determined by difference. The beads left in the conical flasks were thoroughly washed with distilled water for 30 s and dried at 60°C until a constant weight (W_d) was achieved. The amount of herbicide retained on the resin (C_{ad}, $mol\,g^{-1}$) was calculated as:

$$C_{ad} = [C_o V_o - C_{eq}(V_o + \Delta V)]/1000 W_d. \tag{1}$$

Table 2. HPLC conditions.

Conditions	Herbicides		
	Alachlor	Trifluralin	Prometryn
Mobile phase (acetonitrile/H_2O)	60 : 40	70 : 30	70 : 30
Flow rate (mL min^{-1})	1	1.2	1.2
UV detector (λ, nm)	220	254	254
Retention time (min)	9.7	9.2	4.5
Temperature (°C)	30	30	30
Sample volume (μL)	20	20	20

Table 3. Effect of ionic strength on the adsorption of herbicides at pH 3 and $T = 20°C$.

	Ionic strength					
	0.01 M		1 M		2 M	
Herbicide	C_{eq} (mol L^{-1})	C_{ad} (mol g^{-1})	C_{eq} (mol L^{-1})	C_{ad} (mol g^{-1})	C_{eq} (mol L^{-1})	C_{ad} (mol g^{-1})
Alachlor	1.20×10^{-4}	2.52×10^{-5}	0.16×10^{-5}	2.42×10^{-5}	0.37×10^{-5}	3.87×10^{-5}
	0.90×10^{-4}	2.76×10^{-5}	0.16×10^{-4}	4.12×10^{-5}	1.20×10^{-4}	8.14×10^{-5}
	1.00×10^{-4}	3.85×10^{-5}	2.29×10^{-4}	7.70×10^{-5}	6.62×10^{-4}	11.95×10^{-5}
	6.50×10^{-4}	5.10×10^{-5}	1.24×10^{-3}	9.20×10^{-5}	1.60×10^{-3}	16.95×10^{-5}
	12.50×10^{-4}	6.20×10^{-5}	2.27×10^{-3}	11.70×10^{-5}	1.10×10^{-3}	17.00×10^{-5}
Prometryn	0.26×10^{-3}	1.71×10^{-5}	0.32×10^{-4}	3.57×10^{-5}	0.23×10^{-3}	5.18×10^{-5}
	0.36×10^{-3}	2.60×10^{-5}	0.32×10^{-3}	6.11×10^{-5}	0.19×10^{-3}	9.26×10^{-5}
	0.80×10^{-3}	3.29×10^{-5}	1.85×10^{-3}	6.40×10^{-5}	0.99×10^{-3}	15.20×10^{-5}
	1.68×10^{-3}	3.73×10^{-5}	1.10×10^{-3}	7.12×10^{-5}	2.43×10^{-3}	15.69×10^{-5}
	1.85×10^{-3}	3.80×10^{-5}	2.51×10^{-3}	9.04×10^{-5}	3.12×10^{-3}	16.00×10^{-5}
Trifluralin	0.35×10^{-4}	2.52×10^{-5}	0.24×10^{-5}	1.47×10^{-5}	0.30×10^{-6}	2.58×10^{-5}
	1.38×10^{-4}	3.03×10^{-5}	0.84×10^{-5}	3.98×10^{-5}	0.18×10^{-5}	4.96×10^{-5}
	3.00×10^{-4}	3.40×10^{-5}	0.75×10^{-4}	6.30×10^{-5}	0.24×10^{-4}	9.16×10^{-5}
	5.00×10^{-4}	3.45×10^{-5}	0.77×10^{-3}	6.31×10^{-5}	6.11×10^{-4}	9.45×10^{-5}
	7.68×10^{-4}	3.49×10^{-5}	0.50×10^{-3}	6.32×10^{-5}	2.75×10^{-4}	10.40×10^{-5}

Equation (1) is derived from the general equation for the calculation of adsorbate retained on a solid, when initially dry beads are used:

$$C_{ad} = (C_o V_o - C_{eq} V_o)/1000 W_d, \tag{2}$$

where, ΔV (dilution) $= (W_w - W_d)/\rho$ (mL), W_w and W_d are the wet and dry resin weight, respectively (g), V_o is the initial volume of herbicide solution (mL), and ρ is the density of water (g mL^{-1}).

The difference between equations (1) and (2) is the mass calculation (mol) of the adsorbate in the solvent at equilibrium, namely $C_{eq}(V_o + \Delta V)$ (equation (1)) instead of $C_{eq} V_o$ (equation (2)), due to the dilution from the addition of wet beads.

3. Results and discussion

The results of the effect of ionic strength on the adsorption of alachlor, trifluralin, and prometryn on the resin XAD-4 at pH 3 and 6.5 are given in tables 3 and 4, respectively.

Table 4. Effect of ionic strength on the adsorption of herbicides at pH 6.5 and $T = 20°C$.

	Ionic strength					
	0.01 M		1 M		2 M	
Herbicide	C_{eq} (mol L^{-1})	C_{ad} (mol g^{-1})	C_{eq} (mol L^{-1})	C_{ad} (mol g^{-1})	C_{eq} (mol L^{-1})	C_{ad} (mol g^{-1})
Alachlor	0.18×10^{-3}	0.72×10^{-5}	0.68×10^{-4}	7.00×10^{-5}	0.14×10^{-4}	1.56×10^{-5}
	0.34×10^{-3}	2.12×10^{-5}	0.28×10^{-3}	10.40×10^{-5}	0.20×10^{-3}	11.90×10^{-5}
	0.50×10^{-3}	2.15×10^{-5}	1.45×10^{-3}	11.90×10^{-5}	0.71×10^{-3}	13.70×10^{-5}
	0.70×10^{-3}	2.40×10^{-5}	1.83×10^{-3}	13.20×10^{-5}	1.93×10^{-3}	16.80×10^{-5}
	1.60×10^{-3}	2.60×10^{-5}	1.22×10^{-3}	14.22×10^{-5}	1.03×10^{-3}	18.20×10^{-5}
Prometryn	0.19×10^{-3}	3.02×10^{-5}	0.29×10^{-3}	4.90×10^{-5}	0.20×10^{-4}	5.26×10^{-5}
	0.55×10^{-3}	3.40×10^{-5}	0.41×10^{-3}	7.60×10^{-5}	0.75×10^{-4}	12.50×10^{-5}
	1.25×10^{-3}	3.80×10^{-5}	2.69×10^{-3}	8.83×10^{-5}	1.45×10^{-3}	15.15×10^{-5}
	1.55×10^{-3}	4.00×10^{-5}	1.68×10^{-3}	9.50×10^{-5}	3.15×10^{-3}	15.40×10^{-5}
	1.80×10^{-3}	4.31×10^{-5}	3.50×10^{-3}	11.00×10^{-5}	2.93×10^{-3}	16.37×10^{-5}
Trifluralin	0.18×10^{-5}	1.14×10^{-5}	0.30×10^{-5}	3.99×10^{-5}	0.42×10^{-5}	3.31×10^{-5}
	0.18×10^{-4}	2.23×10^{-5}	0.68×10^{-4}	6.40×10^{-5}	0.19×10^{-4}	6.19×10^{-5}
	0.91×10^{-4}	2.27×10^{-5}	0.13×10^{-3}	8.04×10^{-5}	0.15×10^{-4}	7.55×10^{-5}
	0.41×10^{-3}	2.47×10^{-5}	1.03×10^{-3}	8.70×10^{-5}	0.15×10^{-3}	9.62×10^{-5}
	0.83×10^{-3}	2.72×10^{-5}	0.29×10^{-3}	8.71×10^{-5}	0.66×10^{-3}	10.44×10^{-5}

It is observed in all cases that by increasing the ionic strength, the adsorption increases. This is the normal effect of ionic strength for adsorption from aqueous solution onto non-polar hydrophobic adsorbents and, probably, onto polar adsorbents without strongly charged sites [16]. The mechanism of adsorption onto polar and uncharged surfaces, like XAD-4 surface, will be much more complex than that of the non-polar case, since such factors as orientation will be determined by a balance of several forces. The potential forces operating at a polar surface include the ever-present dispersion forces, dipolar interactions, H-bonding and other acid–base interactions. The relative balance between the dispersion forces and the uniquely polar interactions is of supreme importance in determining the mode of organic molecule adsorption. Ionic strength can affect both the solvent power (H-bonding between water molecules and herbicide) and the interactions at the herbicide–resin interface, such as electrostatic forces, H-bonding forces, and repulsive forces between electron-rich aromatic nuclei of adsorbates and adsorbents as well as interactions between adsorbate molecules [10, 16].

Therefore, since the influence of salt on solvent power is to increase the adsorption (the salting-out phenomenon), the higher adsorption of the tested herbicides is partly due to the addition of salt [10, 17]. Furthermore, a reinforcement of some types of attractive interactions should occur, determined by the resin and herbicide structure and the environmental conditions. Since XAD-4 resin molecule contains an electron-rich aromatic nuclei (styrene–divinylbenzene copolymer), it has a pronounced ability to interact by polarization of π electrons with oppositely charged solute molecules [17]. Alachlor and trifluralin molecules also possess an aromatic ring capable of similar interactions (as above). So, it is obvious that the presence of aromatic rings at both sides of the resin–herbicide interface causes repulsive forces to be developed. Sodium chloride ions, interacting by induced dipolar forces with the aromatic π electrons, should decrease the repulsive forces at the herbicide–resin interface, consequently resulting in an increase in adsorption [16]. In the case of prometryn adsorption, because the prometryn molecule consists of a triazine ring with an electronic behaviour similar

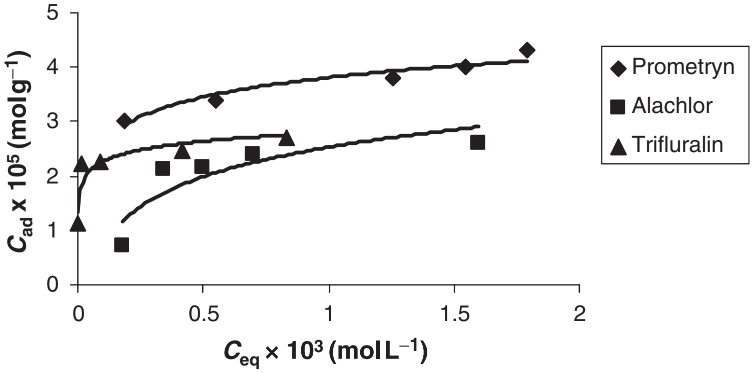


Figure 1. Effect of herbicide structure on adsorption at pH 6.5, XAD-4, ionic strength 0.01 M and $T = 20^\circ$C.

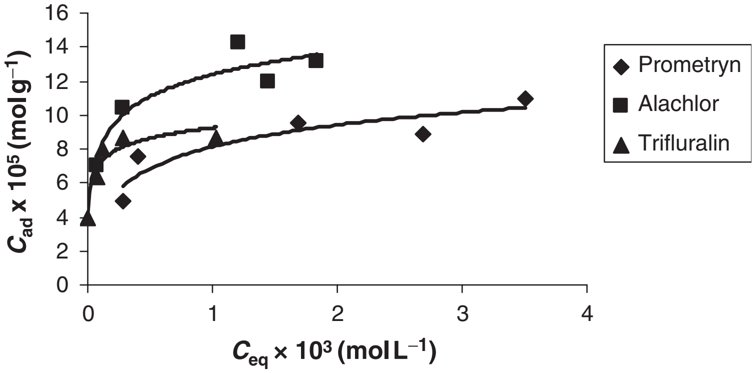


Figure 2. Effect of herbicide structure on adsorption at pH 6.5, XAD-4, ionic strength 1 M and $T = 20^\circ$C.

to that of benzene, a similar mechanism including reduced repulsive forces at the prometryn–XAD-4 interface should exist, by the addition of sodium chloride.

It is evident that the presence of a variety of substituents in the aromatic ring of alachlor and trifluralin molecule, as well as in the triazine ring of prometryn molecule, normally alters, to a different degree for each herbicide, the electronic nature of the rings. In trifluralin, the groups NO_2, CF_3, and $N(CH_2CH_2CH_3)_2$, contributing to a reduced electron density of aromatic ring, should eventually decrease the electron density in the ring. In contrast, the substituents of alachlor and prometryn rings, such as CH_2CH_3 and $NHCH(CH_3)_2$, should eventually increase the electron density of both rings. So, the effect of salt addition is expected to be more pronounced at the alachlor–XAD-4 and prometryn–XAD-4 interface, since the reduction in repulsive forces should be higher. Therefore, the effect of ionic strength for alachlor and prometryn adsorption is more intensive compared with trifluralin adsorption, as illustrated in figures 1–3.

The effect of ionic strength on herbicide adsorption is strongly affected by the solution pH. In the case of alachlor, this effect is illustrated in figure 4. It is observed that the mechanisms of adsorption are influenced by a pH change at a low ionic strength [18], while the pH factor is not significant at higher ionic strength values.

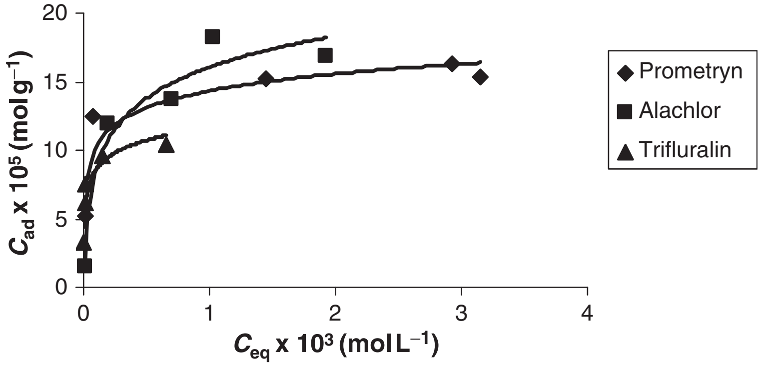


Figure 3. Effect of herbicide structure on adsorption at pH 6.5, XAD-4, ionic strength 2 M and $T = 20°C$.

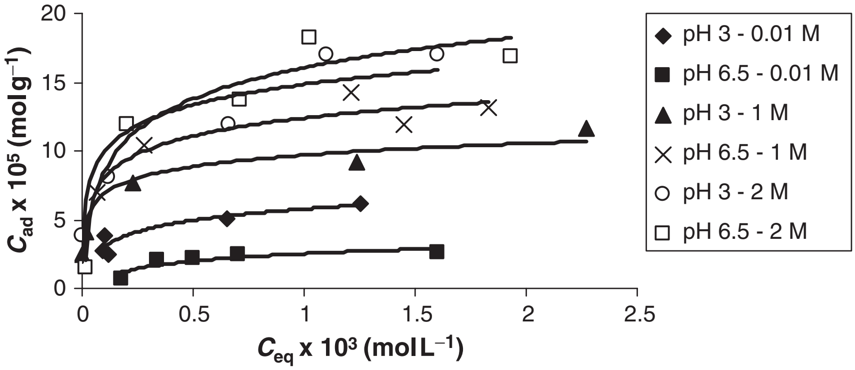


Figure 4. Effect of pH and ionic strength on adsorption of alachlor on XAD-4 at $T = 20°C$.

The higher concentration of counterions determines the adsorption interactions, resulting in saturation at the herbicide–resin interface. The combined effect of ionic strength and pH on herbicide adsorption is shown in figure 5. Herbicide increases in adsorption by increasing the ionic strength are due (except for salting out) to the reduction in repulsive forces between herbicide molecules and adsorbent, thus permitting closer packing [17].

4. Conclusions

Adsorption of alachlor, trifluralin, and prometryn on Amberlite XAD-4 at pH 3 and 6.5 increases by increasing the ionic strength. This effect is more pronounced in alachlor and prometryn adsorption in comparison with trifluralin adsorption. The polar structure of alachlor and prometryn in conjunction with the contribution of their substituents in increasing the electron density of the molecules is responsible for the stronger reduction in repulsive forces, at the polar resin–herbicide interface, caused by the ionic strength. In additition, the phenomenon of salting out is beneficial for

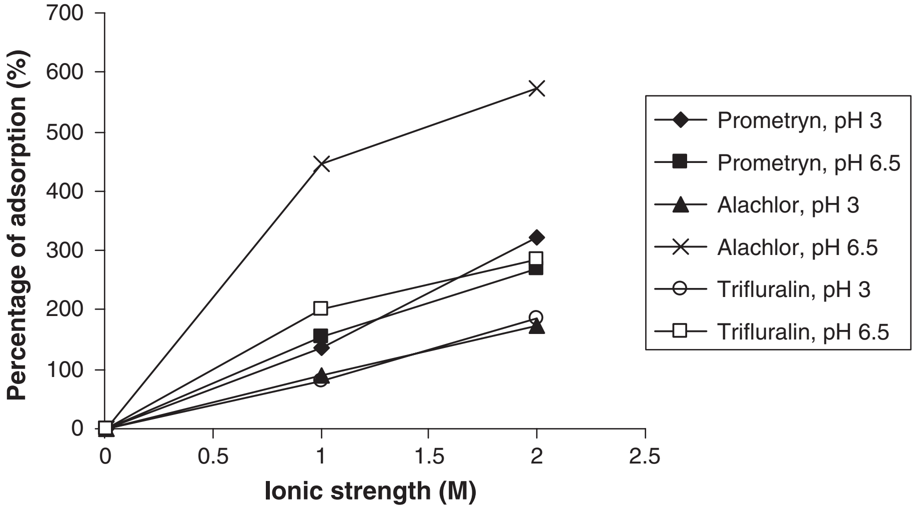


Figure 5. Effect of ionic strength on herbicide adsorption.

a higher adsorption achievement. Adsorption is highly influenced by pH at low ionic strengths, while at higher pH values, the effect of pH is limited.

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