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# Sorption of Pesticides and Herbicides on Highly Polar Polymeric Sorbents

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## ABSTRACT

Six porous copolymers of acrylonitrile (AN)/divinylbenzene (DVB) and methacrylonitrile (MAN)/DVB have been synthesized by the suspension polymerization in the presence of inert diluents. The resulting adsorbents are found to have slightly different specific surface areas (460–720 $m^2$/g for AN/DVB and 560–730 $m^2$/g for MAN/DVB) and contain various amounts of strongly polar nitrile groups. The influence of surface polarity has been studied for the sorption of selected pesticides and herbicides from water. In addition, a series of styrene-divinylbezene resins, namely Hypersol-Macronet™ MN-100 (weakly basic), MN-400 (strongly basic), and MN-200 (unfunctionalized) have been tested for the removal of selected pesticides and herbicides. The sorption of atrazine on

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all studied sorbents is significantly higher than sorption of imazapyr or 2,4-dichlorophenoxyacetic acid. Atrazine sorption on AN/DVB and MAN/DVB resins is in the range of 30–66 mg/g (0.055–0.092 mg/m$^2$) at an equilibrium concentration of 1 mg/L in solution.

*Key Words:* Polar sorbents; Atrazine; Imazapyr; 2,4-Dichlorophenoxyacetic acid; Sorption.

## INTRODUCTION

Many low molecular weight organic compounds are removed from aqueous solutions by adsorption using porous materials such as activated carbon and/or polymeric resins. The driving force of this process is interaction of the solute molecules with the sorbent surface and can be attributed to weak hydrophobic interactions, e.g., van der Waals forces or stronger interactions such as dipole–dipole and hydrogen bonding. For this reason, the interaction between sorbent and sorbate can be modified, changing the character of the sorbent surface. This will significantly influence sorbent capacity and selectivity.

The surface properties of polymers can be controlled by careful choice of the monomers, including the crosslinking agent, or by chemical modification of common polymers, e.g., styrene-divinylbenzene. Masque et al.[1] have introduced o-carboxybenzoyl groups onto the surface of three different styrene-divinylbenzene copolymers, and the modified materials were used in solid phase extraction of polar compounds. It was found that increased surface polarity resulted in a marked increase of the percentage recovery of resorcinol and phenol. Recovery of more hydrophobic sorbates from dilute (0.5–5 μg/L) solution was not significantly changed. The same authors also investigated the sorptive properties of other chemically modified sorbents containing acetyl[2] and benzoyl groups,[3] while Fritz, Dumont, and Schmidt have obtained solid phases with hydroxymethyl functionalities.[4]

Another method of altering the surface properties is copolymerization of appropriate monomers, containing suitable functional group(s). Some of these polymers are commercially available, e.g., Amberlite XAD-7 and Chromosorb 104, that have ester and nitrile groups, respectively. Also, other copolymers with nitrile groups, i.e., copolymers of acrylonitrile and divinylbenzene (designated AN/DVB)[5,6] and methacrylonitrile and divinylbenzene (designated MAN/DVB)[7] have been synthesized and used as sorbents. The sorptive properties of AN/DVB copolymers have been compared to conventional styrene/divinylbenzene copolymers (designated St/DVB).[5,6] It was observed that the distribution coefficient of various phenols was 2–3 times higher on AN/DVB compared with St/DVB sorbents despite the fact that porosity (ca. 48%, specific surface area (465 and 490 $m^2$/g), and average pore diameter (4.6 and 4.5 nm)) were very similar. The sorption of phenol on mesoporous MAN/DVB copolymers reached a maximum value when polymer is crosslinked with 30% and 40% wt. of divinylbenzene (specific surface area 433 and 500 $m^2$/g, respectively). Phenol sorption decreased by 10–15% for the sample with the highest specific surface area of 552 $m^2$/g, but having lower content of polar groups.[7] Thus, it can be concluded that a large specific surface area and a large proportion of strongly polar functional groups are equally important for the sorption of polar sorbates (e.g., phenol and its derivatives). This has been confirmed in our recent paper,[8] where it was shown that sorbents with a large proportion of strongly polar, nitrile groups performed much better than styrene/divinylbenzene copolymers.

Having the above in mind we decided to apply AN/DVB and MAN/DVB sorbents to the removal of other sorbates, which are capable of dipole–dipole interaction and hydrogen bonding. Atrazine (6-chloro-$N^2$-ethyl-$N^4$-isopropyl-1,3,5-triazine-2,4-diamine), imazapyr [(2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid)], and 2,4-D (2,4-dichlorophenoxyacetic acid) have been selected as they represent different classes of pesticides and herbicides. Removal of these compounds was already reported in the literature using both carbon,[9–11] polymeric resins,[12–14] and other adsorbents.[15–17]

The aim of the present work is to determine the extent of sorption of selected pesticides (atrazine) and herbicides (imazapyr and 2,4-dichlorophenoxyacetic acid) on the acrylonitrile/divinylbenzene and methacrylonitrile/-divinylbenzene sorbents. In addition, commercially available styrene-divinylbenzene resins, namely Hypersol-Macronet™ MN-100 (weakly basic), MN-400 (strongly basic), and MN-200 (unfunctionalized) have been tested for the removal of atrazine and imazapyr from water.

## EXPERIMENTAL

Copolymers of acrylonitrile (AN) and divinylbenzene (containing 80% wt. of isomers, Aldrich) (DVB) as well as copolymers of methacrylonitrile (MAN) and DVB were prepared by suspension polymerization using 0.5% wt. of benzoyl peroxide as initiator. Three levels of crosslinking were used in both cases: 50%, 60%, and 70% wt. of DVB. Polymerization was carried out according to the previously published procedure.[8] After polymerization, the beads were washed with hot water, water, and acetone, and then dried. The polymer was preswollen in toluene and extracted with this solvent for 12 h in a Soxhlet apparatus, then washed successively with pure solvents and solvent mixtures having a gradual increase in solubility parameter, i.e., toluene/acetone, acetone, acetone/methanol, methanol, methanol/water, and finally with plenty of distilled water. Water-swollen polymers were wet-sieved and fraction 0,32–0,6 mm was used in subsequent sorption experiments. All Macronet resins were supplied courtesy of Purolite International Limited.

The sorption isotherms of selected pesticides and herbicides have been determined. A batch method was used for atrazine and imazapyr. Five hundred mL of a 10 mg/L solution of the sorbate was contacted in 500 mL amber Winchester bottles (containing PTFE liners) with different amounts of the given sorbent for 5 days at 25°C, shaking the bottles in an incubator shaker at $100\,\mathrm{min}^{-1}$. Subsequently, the sorbent was removed by filtration and the pesticide equilibrium concentration was measured using HPLC. A Hewlett Packard 1100 series HPLC system consisting of a binary pump, autosampler, column thermostat, and diode array detector was used to analyze the compounds. A Genesis column (4 μm, 150 × 3 mm) was used combined with a 1 cm Genesis guard column supplied by Jones Chromatography. Two methods were required to analyze imazapyr and atrazine. HPLC measurement conditions for atrazine were: wavelength 222 nm, flow rate 0.88 mL/min, eluant—50% 10 mM potassium dihydrogen phosphate pH 3.3 adjusted with phosphoric acid and 50% acetonitrile, injection volume 10 μL, column temperature 38°C. The measurement conditions for imazapyr were: wavelength 204 nm, flow rate 0.40 mL/min, eluant—80% and 10 mM potassium dihydrogen phosphate pH 3.3 adjusted with phosphoric acid and 20% acetonitrile, remaining parameters as for atrazine. Sorption of 2,4-dichlorophenoxyacetic acid was measured by contacting 10 mL of 0.0005 M solution in a 25 mL Erlenmeyer flask with an appropriate amount of swollen and centrifuged polymer. After shaking at room temperature for 24 h, the polymer was separated and the concentration of herbicide measured using UV/VIS spectrophotometer with wavelength set at 263 nm.

## RESULTS AND DISCUSSION

The aim of the present work is to study the removal of specific pesticide and herbicides from aqueous solution, i.e., derivatives of triazine and nicotinic acid and 2,4-dichlorophenoxyacetic acid by adsorption on newly synthesized AN/DVB and MAN/DVB polymers. These compounds were chosen for two reasons. Firstly, their concentration in the environment is strictly limited and therefore methods of removal from ground and surface water must be highly effective, and secondly, because these molecules contain polar fragments within their structure. This suggests that strongly polar sorbents may be more efficient sorbents than traditional styrene/divinylbenzene copolymers. Commercial weakly and strongly basic as well as unfunctionalized styrene-divinylbenzene were tested for comparison purposes.

In the present work, we decided to use previously developed AN/DVB and MAN/DVB sorbents.[8] These materials were obtained from DVB of higher purity—80% wt. of m- and p-divinylbenzene, which is commercially available and hence we were able to produce materials with high content of strongly polar -CN groups per g of polymer.

In each series of polymers, i.e., AN/DVB and MAN/DVB, the specific surface area increases with increased degree of crosslinking and reaches values in excess of 700 $m^2$/g for polymers containing 70% of DVB (see Table 1). The calculated mean pore diameter is in the range of 7.0–9.4 nm and similar in all cases indicating a mesoporous structure. The pore volume gradually increases from about 1.0 $cm^3$/g to more than 1.5 $cm^3$/g in the AN/DVB copolymers, whereas is almost constant for MAN/DVB. The pore volume values for the bimodal MN-100, MN-200, and MN-400 resins are between 1–1.1 $cm^3$/g and the mean pore diameter is 1.5 nm (in micropore range) and 85–90 nm (in mesopore range). Figs. 1b and 2b show the incremental pore volume and incremental pore area of AN and MAN resins, respectively. Incremental pore volume data for Macronet resins has been published previously[14] and it is also presented for comparison in Fig. 3b. As can be seen, the lower crosslinked sorbent-50AN, has an average pore diameter of ca. 2.3 nm. It is these pores that contribute most to the specific surface area. The two other AN resins also

***Table 1.*** Selected atrazine and imazapyr sorption results at $C_{eq}$ 1 mg/L.

| | Atrazine | | Imazapyr | | BET surface area |
|---|---|---|---|---|---|
| Sorbent | mg/g | mg/$m^2$ | mg/g | mg/$m^2$ | $m^2$/g |
| MN100 | 48.8 | 0.053 | 29.0 | 0.032 | 922 |
| MN200 | 31.0 | 0.029 | 20.0 | 0.019 | 1072 |
| MN400 | 21.8 | 0.023 | 27.0 | 0.028 | 950 |
| 50AN/DVB | 30.0 | 0.065 | 4.0[a] | 0.009[a] | 460 |
| 60AN/DVB | 31.0 | 0.055 | 5.6[a] | 0.010[a] | 560 |
| 70AN/DVB | 66.0 | 0.092 | 11.6[a] | 0.016[a] | 720 |
| 50MAN/DVB | 36.0 | 0.064 | 3.0[a] | 0.005[a] | 560 |
| 60MAN/DVB | 51.0 | 0.090 | 7.2[a] | 0.013[a] | 570 |
| 70MAN/DVB | 64.0 | 0.088 | 11.0[a] | 0.015[a] | 730 |

[a] Extrapolated data.

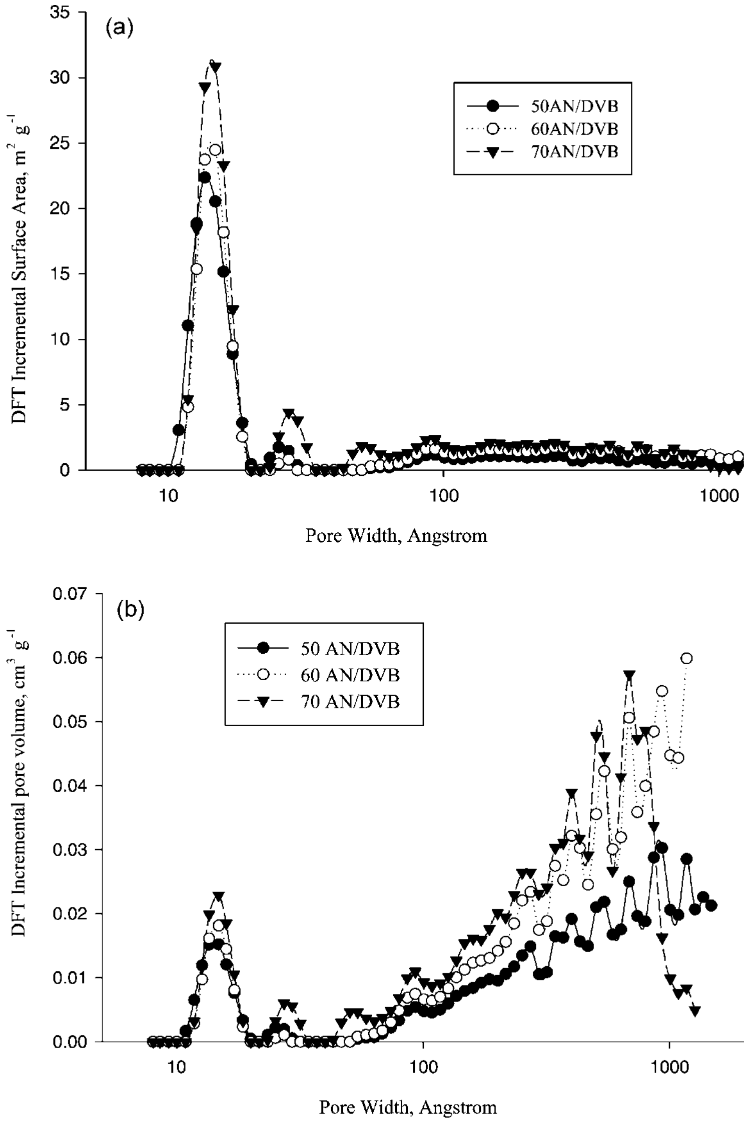


***Figure 1.*** Incremental pore area (a) and incremental pore volume (b) for AN series of sorbents.

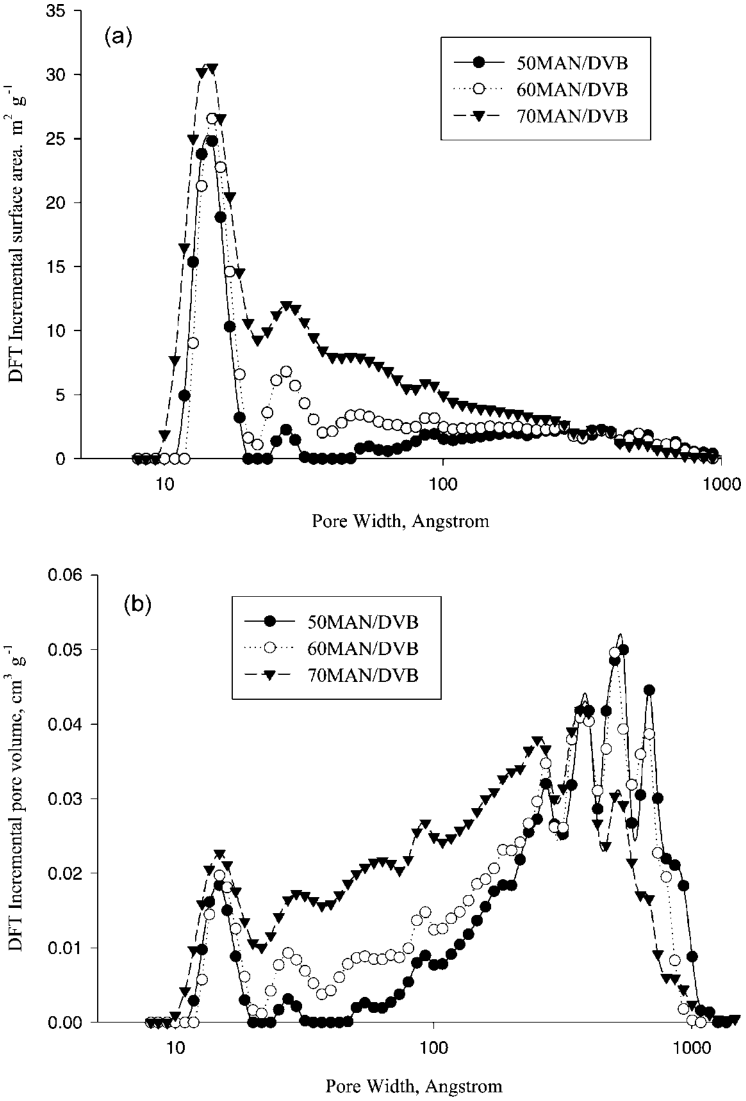


***Figure 2.*** Incremental pore area (a) and incremental pore volume (b) for MAN series of sorbents.

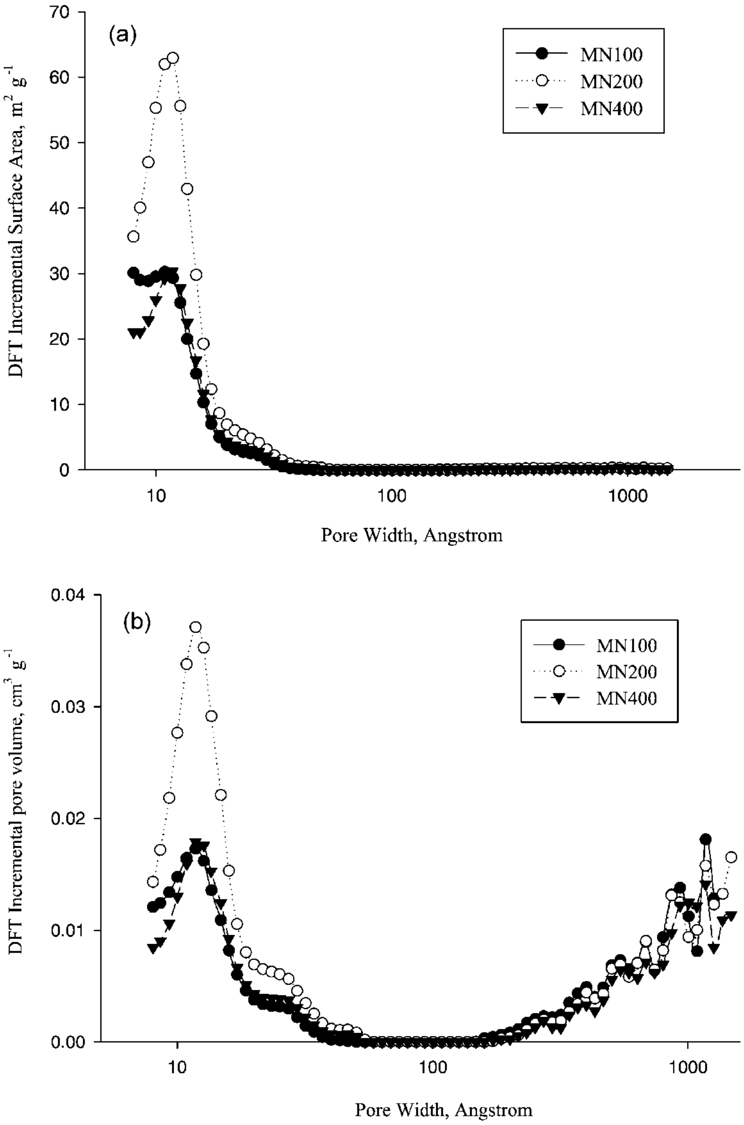


***Figure 3.*** Incremental pore area (a) and incremental pore volume (b) for Macronet$^{TM}$ sorbents.

possess the same average pore diameter but they have additional pores that contribute significantly to the total surface area (see Table 1 for comparison of the surface areas). These additional pores are in the range 50–70 nm in the case of sorbent 60AN and 30–50 nm in the case of sorbent 70AN. Accordingly, the most significant contribution to the total pore volume (Fig. 1b) can be attributed to pores of increasing diameter for 50AN, 60AN, and 70AN. In the case of the MAN series, the situation is slightly different. In this case, the total surface area can be attributed to pores in two size ranges, i.e., 2–3 nm and 38–46 nm for all the resins. These resins are bimodal; the mesopores in the 2–3 nm range are responsible for the high surface area and hence for the adsorption capacity, whereas the large pores in the 38–46 nm are transport pores allowing access to the smaller pores.

The adsorption of atrazine, imazapyr, and 2,4-dichlorophenoxyacetic acid was investigated on AN/DVB and MAN/DVB resins, and sorption isotherms were obtained in the concentration range 0–120 mg/L depending on the sorbate. Figures 4A and 4B show atrazine sorption isotherms for AN resin and Figs. 4a and 4b for MAN resins. It can be seen that atrazine sorption is quite high even at low solution concentration. Sorption of atrazine increases at higher degrees of crosslinking, probably due to higher specific surface area.[8] This effect is particularly strong in the AN series, where sorption reaches 65 mg of atrazine per gram of 70AN sorbent at 1 mg/L equilibrium concentration and is about twice the uptake in comparison with the other two AN sorbents (see Fig. 4A and Table 1). Differences in atrazine sorption on MAN sorbents, although detectable, are less significant. Figure 4B shows the normalized sorption i.e., sorption referred to the amount of sorbate deposited on 1 $m^2$ of sorbent. It is seen that sorption differences are less pronounced and that the normalized sorption of atrazine on 50AN, having smaller specific surface area (450 $m^2/g$) but higher content of nitrile groups, is greater than normalized atrazine sorption on 60AN. The atrazine sorption values for 50AN/DVB and 60AN/DVB on a per gram basis are about the same; however, on a per square meter basis, 50AN/DVB shows a 17.5% higher sorption of atrazine over 60AN/DVB at an equilibrium concentration of 1 mg/L. This result highlights the importance of the surface polarity on the sorption of atrazine. A similar effect is also observed for the MAN series of resins, where the 70MAN/DVB displays a higher atrazine sorption value on the per gram basis compared with 60MAN/DVB. However, the normalized sorption of atrazine on 60MAN and 70MAN resins is almost the same (see Table 1). The atrazine sorption data for Macronet resins suggests that the less polar styrene-divinylbenzene surface shows lower affinity (about half) towards atrazine compared with the more polar resins i.e., 70AN/DVB and 70MAN/DVB (see Table 1). Some differences between the atrazine affinity for MN-100,

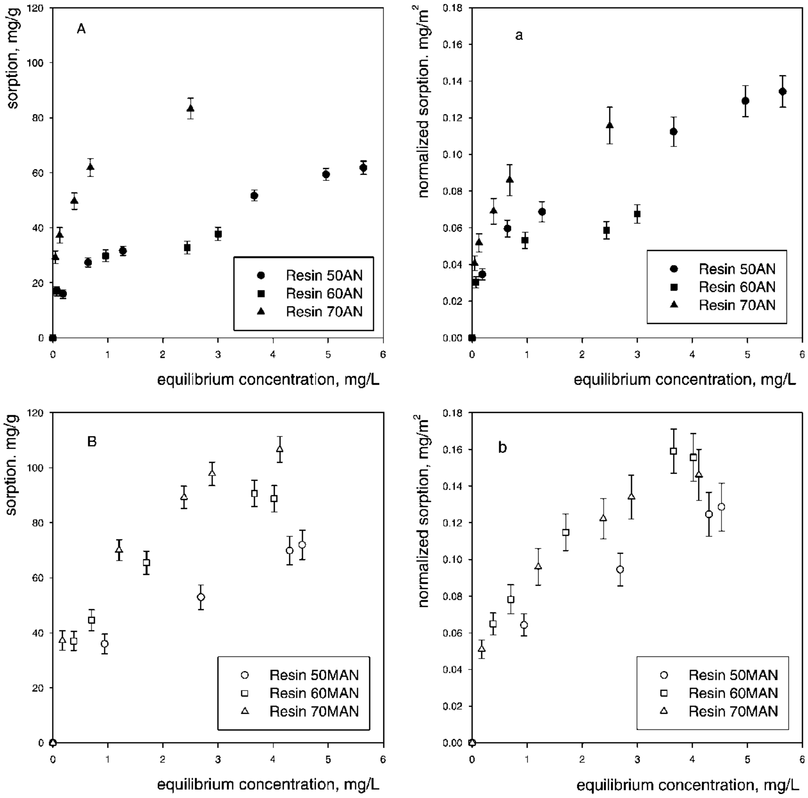


***Figure 4.*** Sorption isotherms of atrazine on AN and MAN resins.

MN-200, and MN-400 were observed, although our earlier work carried out at much lower pesticide concentrations (ppb range) suggested little difference between the resins.[13] Among Macronet sorbents the highest atrazine sorption, in mg of atrazine per square meter is shown in the case of MN 100. This sorbent has weakly basic character and as such has the ability to interact with atrazine molecules through either nitrogen atom in a 3 position or chlorine atom in a 6 position. Other Macronet sorbents-MN 200 (unfunctionalized) and MN 400 (strongly basic) adsorb ca. two times less atrazine per square meter than MN 100.

The favorable adsorption of atrazine, manifested by isotherms concave upwards, as opposed to unfavorable adsorption of two other compounds (imazapyr and 2,4-dichlorophenoxyacetic acid) may be caused by much lower solubility of the former compound in aqueous solutions. Another possible explanation is atrazine ability to form stronger intermolecular hydrogen bonds between pairs of nitrogen atoms in which triazine nitrogens in 3 position serve as acceptors of hydrogens originating in side amino groups.

Figures 5A and 5B show the sorption isotherms of imazapyr on the AN series of resins and Figs. 5a and 5b on the MAN series. Sorption is much weaker on both the AN and MAN sorbents for this compound as compared to atrazine. It appears that sorption is almost directly proportional to the equilibrium concentration of pesticide in solution but uptake is much lower and does not exceed about 12 mg of imazapyr per gram of sorbent (see Figs. 5A and 5a). The normalized sorption (Figs. 5B and b) shows that sorption is highest on both polymers with higher specific surface area. Sorption is lower and comparable on all polymers with 50% and 60% degree of crosslinking

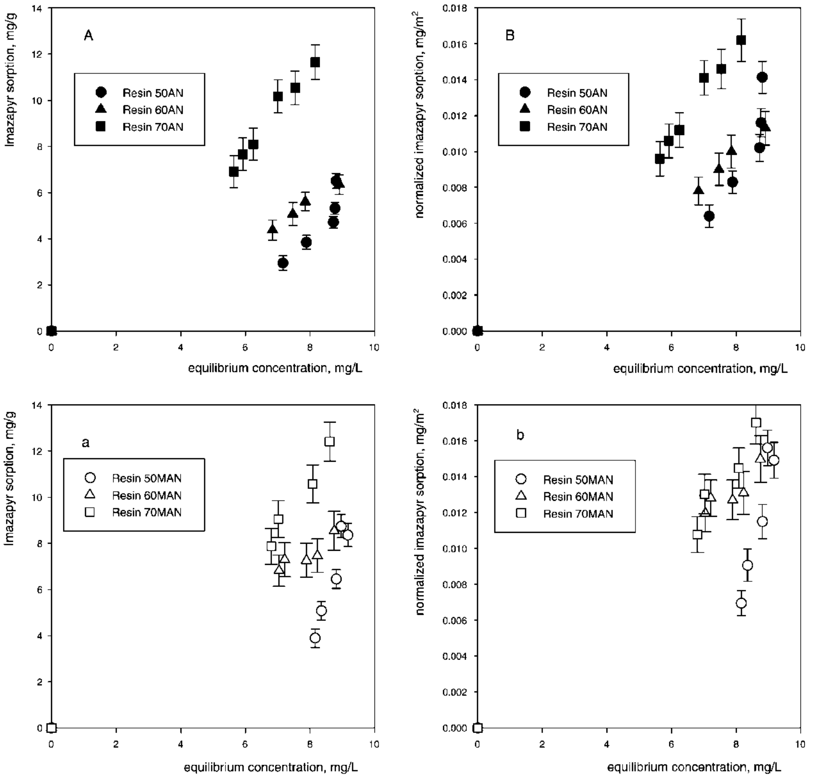
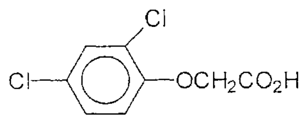


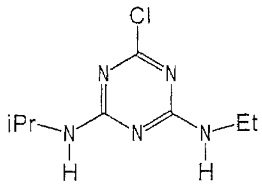
***Figure 5.*** Sorption isotherms of imazapyr on AN and MAN resins.

(50AN, 60AN, 50MAN, and 60MAN). The uptake of imazapyr is about 10 times less than atrazine in a comparable solution concentration range. This may be attributed to the greater hydrophilic character of the former compound. Imazapyr is dissociated and highly hydrated at near-neutral pH conditions of natural water (see Fig. 6). Imazapyr sorption by the Macronet resins is higher in comparison with the AN/DVB and MAN/DVB resins on a per gram as well as on a normalized basis. The functionalized MN-100 and MN-400 show greater affinity for imazapyr than the unfunctionalized MN-200 resin (see Table 1). At neutral pH values, the more positively charged surface of weakly (MN-100) and strongly basic MN-400 resins may result in stronger interactions with the dissociated carboxylate group of imazapyr (see Fig. 6).

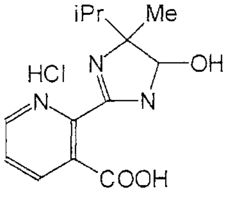
Figures 7A and 7a give sorption isotherms of 2,4-dichlorophenoxycetic acid and also show that sorption is low and comparable to the uptake of imazapyr. After normalization of the sorption values, the differences between



Structure of 2,4-dichlorophenoxyacetic acid



Structure of atrazine



Structure of imazapyr

*Figure 6.* Scheme of the structures of used compounds.

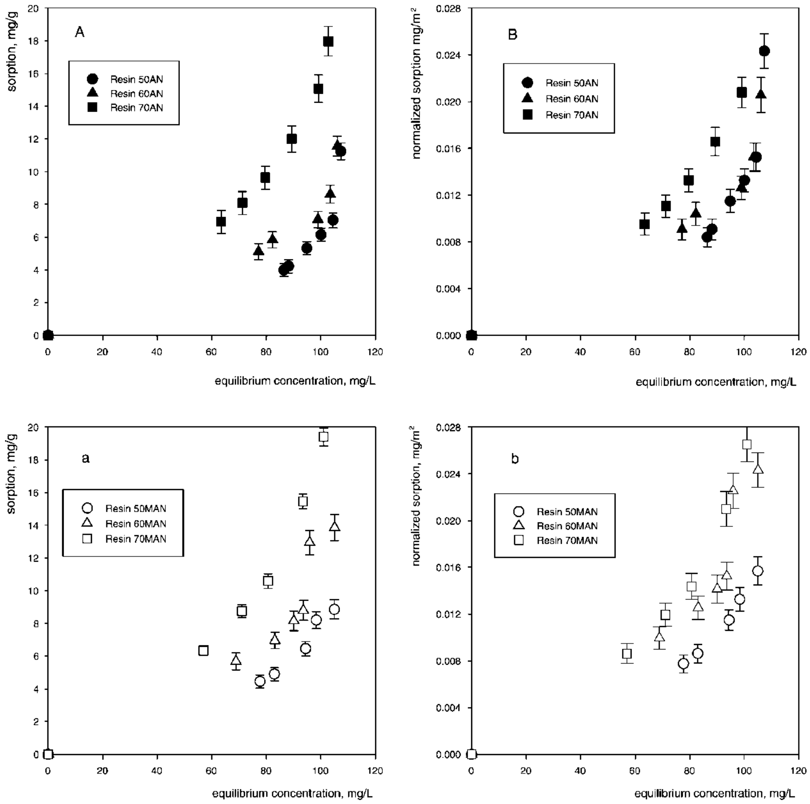


*Figure 7.* Sorption isotherms of 2,4-dichlorophenoxyacetic acid on AN and MAN resins.

AN and MAN sorbents are less pronounced. This further confirms that part of the 2,4-dichlorophenoxyacetic acid uptake is due to the presence of polar groups on the surface of polymers. Normalized sorption is almost the same for 50 and 60AN resins and 60 and 70MAN resins despite their different specific surface areas.

## CONCLUSIONS

It can be concluded that the sorption of atrazine, imazapyr, and 2,4-dichlorophenoxyacetic acid on AN and MAN polymers is largely dependent on the hydrophilicity of these compounds and is greatest for the least hydrophilic compound, namely atrazine. Maximum sorption of atrazine is about 90–100 mg/g from dilute aqueous solutions on both AN and MAN sorbents. Two other more water soluble compounds, i.e., imazapyr and 2,4-dichlorophenoxyacetic acid are significantly less adsorbed; by a factor of almost 10. The effect of polar, surface nitrile groups is more pronounced in AN series of polymers and this effect decreases with an increase in the hydrophilic character of sorbates.

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