

# NEW ANIONIC EXCHANGE RESIN BASED ON QUATERNARY AMMONIUM SALT ADSORBED ON ACTIVATED CARBON

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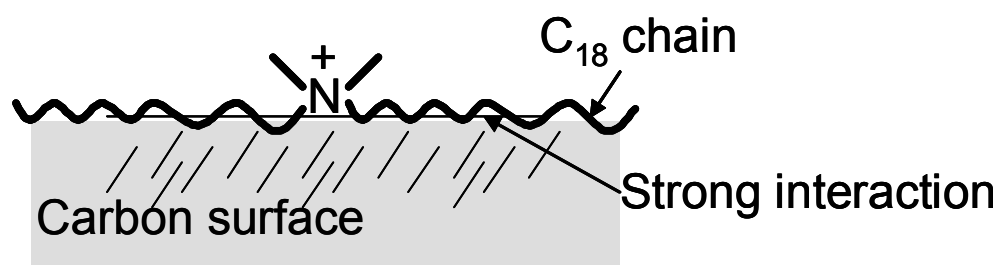
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## Introduction

Anionic exchange resins are polymeric materials, usually a styrene-divinylbenzene copolymer, containing positive charges as  $-N(CH_3)_3^+$  groups in their structure. These resins can efficiently adsorb negatively species from aqueous effluents and have several technological and environmental applications. On the other hand, these materials present a high cost mainly due to the difficulty in their preparation which involves many complex synthetic steps, for instance Friedel-Crafts alkylation, amination and methylation [1,2].

In this work a new type of anionic resin was produced by simply impregnation of a quaternary ammonium salt QAS,  $(C_{18}H_{37})_2(CH_3)_2N^+Cl^-$ , on a high surface area activated carbon. The process is very simple, using low cost commercially available QAS and does not involve complex chemical functionalization. The QAS can be highly dispersed on the carbon and should strongly interact with its surface by the hydrophobic  $C_{18}$  chains (Scheme 1).



Scheme 1. QAS,  $(C_{18}H_{37})_2(CH_3)_2N^+Cl^-$  interaction with carbon surface.

## Experimental

The anionic exchange resin was prepared by impregnation of quaternary ammonium salt QAS,  $(C_{18}H_{37})_2(CH_3)_2N^+Cl^-$ , on activated carbon (Aldrich - Norit) from an isopropanol solution at 10, 20, 30 e 40 wt% of QAS. These materials have been characterized by IR, TG and BET adsorption of  $N_2$  at 77 K analyses. The adsorption tests were carried out at room temperature with 25 mg of the adsorbent with 20 mL of

two different anions solutions:  $\text{HO}^-$  as a model of inorganic anions and the dye Indigo Carmine (IC) as a model of organic anion with concentrations in the range 5 up to 1000  $\text{mg L}^{-1}$ . After a period of 24 h, the  $\text{HO}^-$  was determined by titration and the IC by spectrophotometric measurements.

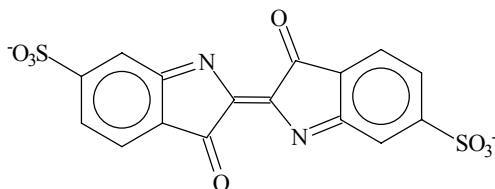
## Results and Discussion

TG analyses showed that the composites QAS/carbon are thermally stable up to  $170^\circ\text{C}$ . In the temperature range  $180\text{--}330^\circ\text{C}$  the ammonium salt completely decomposes and this weight loss was used to confirm the QAS concentration on the carbon surface (Table 1). The BET areas for the different QAS/carbon composites are also shown in Table 1.

It can be observed that the surface area of the original carbon,  $649 \text{ m}^2 \text{ g}^{-1}$  is strongly reduced to  $242 \text{ m}^2 \text{ g}^{-1}$  with only 10% of QAS. Pore distribution analyses suggest that the QAS molecules are occupying and blocking all the porous structure of the carbon adsorbent. At 40 wt% of QAS the surface area of the material is reduced to only  $6 \text{ m}^2 \text{ g}^{-1}$ .

Sample	BET area ( $\text{m}^2 \text{ g}^{-1}$ )
AC original	649
QAS 10 wt%	242
QAS 20 wt%	101
QAS 30 wt%	30
QAS 40 wt%	6

The adsorption isotherms for the two anions model species, *i.e.*  $\text{HO}^-$  and  $\text{IC}^{2-}$  (Scheme 2), have been expressed as weight of NaOH by the weight of carbon and by the weight of QAS.



Scheme 2. Indigo Carmine ( $\text{IC}^{2-}$ ) structure.

The results for the adsorption of  $\text{HO}^-$  are shown in Figures 1 and 2.

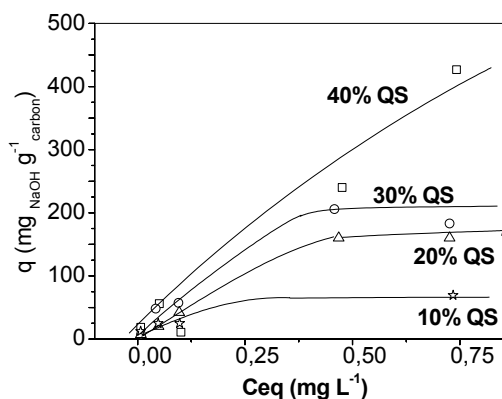


Figure 1 Adsorption isotherm for  $\text{HO}^-$  normalized by the carbon weight.

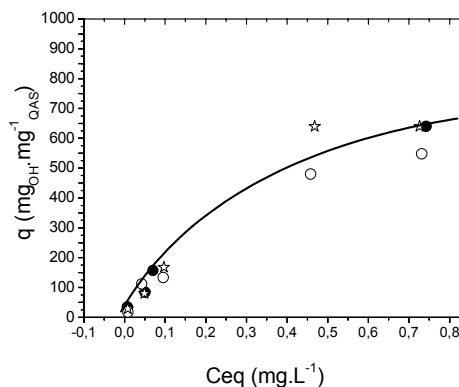


Figure 2. Adsorption isotherm for  $\text{HO}^-$  normalized by the QAS weight.

It can be observed from Figure 1 that as the QAS is added to the carbon, the amount of  $\text{HO}^-$  adsorbed significantly increases even with a strong decrease on the carbon surface area. Figure 2 shows that the amount of  $\text{HO}^-$  adsorbed depends mainly on the concentration of QAS.

Similar results have been obtained for the dye  $\text{IC}^{2-}$  (Figure 3 and 4) which increases its amount adsorbed on carbon as the QAS content increased.

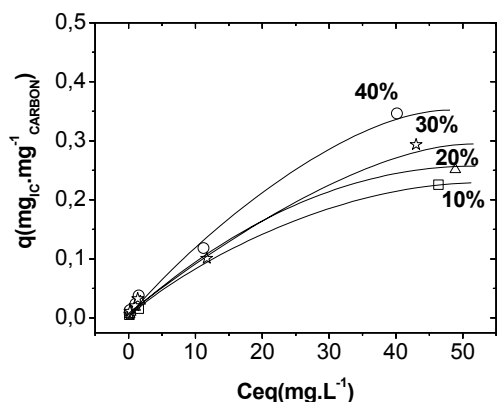


Figure 3. Adsorption isotherm for IC normalized by the carbon weight.

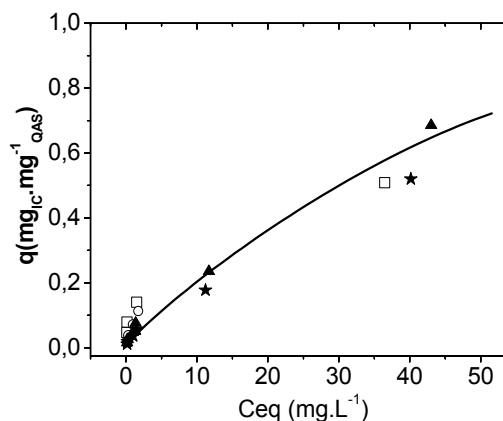
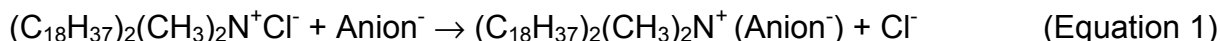


Figure 4. Adsorption isotherm for IC normalized by the QAS weight.

The preliminary results presented in this work suggest that the increase in the adsorption capacity of anionic species on carbon containing QAS  $(\text{C}_{18}\text{H}_{37})_2(\text{CH}_3)_2\text{N}^+\text{Cl}^-$  is likely related to an anion exchange process (Equation 1)



## Conclusion

The presence of the QAS on the activated carbon surface strongly increases the adsorption of anionic species. This increase is related to an ion exchange phenomenon rather than an adsorption on the carbon pores. The composite preparation is very simple and uses the low cost QAS  $(\text{C}_{18}\text{H}_{37})_2(\text{CH}_3)_2\text{N}^+\text{Cl}^-$ .

## References

- [1] Otmer, K. (ed), *Encyclopedia of Chemical Technology*, John Wiley & Sons, Vol 13, New York, 1981.
- [2] Els ER, Lorenzen L and Aldrich C, *Minerals Eng.*, 2000; 13: 401.