Equilibrium and kinetics of nitrate removal by protonated cross-linked chitosan

K Jaafari[1], S Elmaleh[2], J Coma[2]* and K Benkhouja[1]
[1] Groupe de Magnétochimie, Céramiques et Membranes, Faculté des Sciences, Université Chouaïb Doukkali, El Jadida, Morocco
[2] UMR 5569, UM II/CNRS/IRD, Hydrosciences Montpellier, Equipe Génie des Procédés, CC 24, Université Montpellier II, 34095 Montpellier Cedex 5, France

Abstract

Nitrate, contained in surface or groundwater, can be removed by sorption on protonated cross-linked chitosan gel beads. The sorption capacity is pH-dependent and large enough to meet the standard of drinkable water. The isothermal equilibrium curves are straight lines, which implies that the removal is independent of the initial concentration. The main reactive process, which probably depends on the secondary ammonium groups, involves the total bead volume and not only its surface. If required, the sorption capacity is easily recovered by increasing the pH to 12. The main competitor is fluoride but, even in its presence, the sorption capacity of nitrate remains significant. The sorption kinetics, which can be represented by a mass transfer equation, is not limited by pore or by film diffusion.

Introduction

Water resources are, in many countries, heavily polluted by nitrate (Laigla et al., 1990). Nitrate concentration in groundwater or surface freshwater reaches, in some places, more than 100 mg/l. The actual European standard, of less than 50 mg/l in drinkable water, could become more stringent (25 mg/l). The major concern is the blue-baby syndrome resulting from the conversion of haemoglobin into methaemoglobin, which cannot carry oxygen (Golden and Weinstein, 1998). If more than half the haemoglobin is converted, death is likely. Moreover, the adverse effects on adults are not well documented.

Nitrate removal is hampered by its low reactivity. Two treatment techniques are currently used: biological denitrification and ion exchange. Biological denitrification (Richard and Leprince, 1980) requires a carbonaceous substrate and a subsequent polishing treatment like filtration and disinfection. This technique, which is not efficient at a temperature of lower than 7°C, is carried out for groundwater which is constantly at a temperature of around 12°C. Treatment by an ion-exchange resin replaces nitrate by chloride (Deguin, 1988). The resin retains also some sulphate and hydrogen-carbonate, inducing significant changes in the water composition and an increase of the chloride concentration. Moreover, the disposal of the concentrated effluent, obtained after regeneration, should be cautiously considered. Of course electrodialysis or reverse osmosis could also remove nitrate, but their applications are actually hampered by their high cost.

Chitosan is a natural product derived by desacetylation from the polysaccharide chitin. Chitin is found in the exo-skeletons of shrimp, crab and other shellfish. Thanks to its exceptional properties, chitin protects these animals in their natural environment and its applications are growing in a large variety of other fields, e. g. carrier for immobilised cells, artificial skin, membrane synthesis, etc. (Milot, 1998). Chitosan gel beads proved to be a particularly interesting adsorbent in the field of industrial wastewater treatment for the removal of heavy metals (Milot, 1998). However, no reference was found about its capacity to remove nitrate but the presence of amino groups (Muzzarelli, 1977), particularly in cross-linked chitosan, could favour anion adsorption. Considering that chitosan is a soil conditioner that is able to prevent crop diseases (El Ghaout et al., 1992), saturated chitosan could be used as a fertiliser that slowly liberates nitrate. This work is focused on the feasibility of nitrate removal by cross-linked chitosan gel beads.

Experimental

Chitosan gel beads were made by means of the following procedure: chitosan powder, provided by France Chitine, was dissolved in an acetic acid solution of same concentration as the solid (3.5% mass). The solution was then pumped through a hypodermic needle allowing drops to fall down into a tank containing a 2 M NaOH solution. Heterogeneous precipitation induced the formation of highly porous spherical gel beads, which settled at the bottom of the tank. Injecting air, at different flow-rates, around the falling drop allowed varying the bead size. After 12 h, the beads were washed with distilled water in order to reach neutrality. Cross-linked gel beads were obtained after 24 h residence time in a glutaraldehyde solution (5 g/g dry chitosan) (Yoshida et al., 1993). The beads were then cautiously washed with distilled water. The material (100 g/l beads) was protonated by 30-min gentle stirring in a HCl solution the concentration of which conditioned the equilibrium pH of the sorption runs.

Potentiometric studies of the different gels were carried out with 100 g/l beads in a 0.3 N HCl solution. The pH was measured as a function of the added volume (micro-drops) of 0.5 N NaOH.

All the equilibrium and kinetics runs were carried out in 0.5 l batch reactors, mechanically stirred, at 80 RPM in current operation. Equilibrium was reached after 20 to 30 min. Saline solutions were prepared with $NaNO_3$, Na_2SO_4, NaCl and NaF dissolved in distilled or tap water free of nitrate. Contaminated surface or groundwater from the Montpellier region, in France, was also tested. All the runs were carried out at room temperature which was maintained at 20°C. Nitrate concentration was determined by the spectro-

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* To whom all correspondence should be addressed.
☎33 4 67 144626; fax 33 4 67 144626; e-mail: coma@univ-montp2.fr

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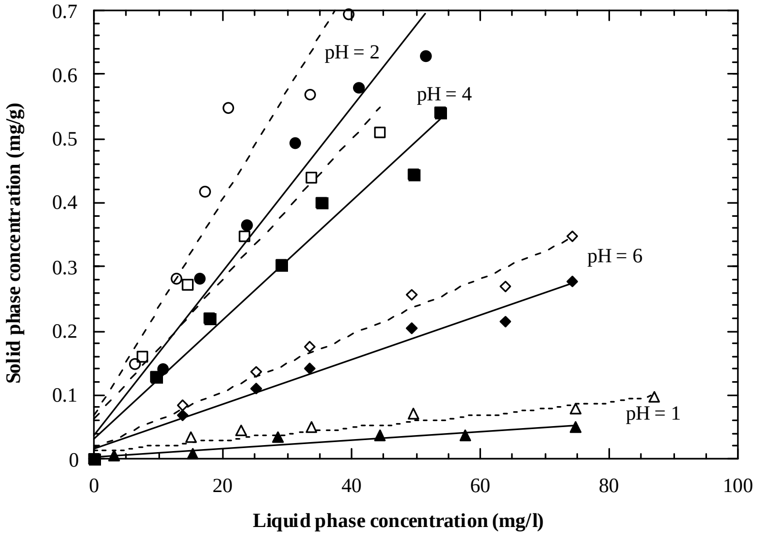

Figure 1
Equilibrium curves at different pH for tap water (full lines) and distilled water (dotted lines) (4.5 mm gel beads)

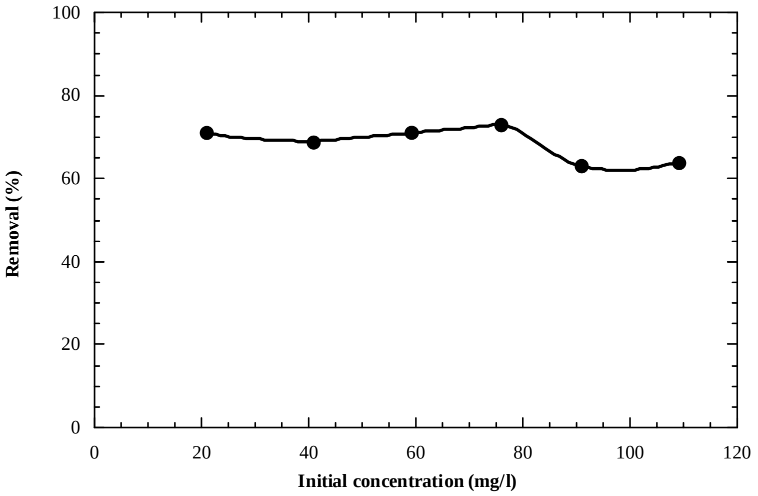

Figure 2
Removal against initial concentration (distilled water, pH = 4)

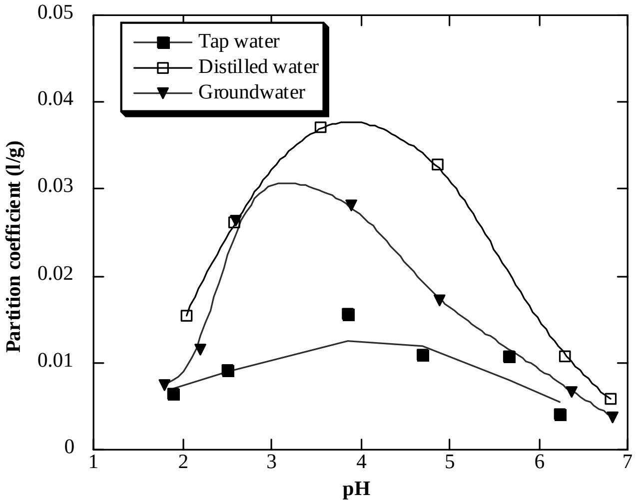

Figure 3
Partition coefficient against pH for different types of water (4.5 mm gel beads)

photometric technique with 5 % accuracy (Spectrophotometer HACH DR 2000 and Nitraver reagent). pH was monitored with a WTW pH 95 pH-meter. The range of nitrate concentration corresponded to polluted surface and groundwater.

Results and discussion

Sorption equilibrium

The nitrate concentration q_e retained on the solid phase, at equilibrium, was calculated by a mass balance between the initial and final states:

$$q_e = \frac{C_0 - C_e}{\rho} \qquad (1)$$

where:

ρ is the ratio between the sorbent mass and the liquid volume

C_0 and C_e being respectively the initial and equilibrium concentrations.

In the studied range of nitrate concentrations, the equilibrium curves were straight lines whose slope depended on final pH (Fig. 1). Straight-line equilibrium curves imply that the removal does not depend on the initial concentration. This is easily demonstrated by combining the mass balance (1) and the equation of an isotherm straight-line:

$$q_e = mC_e \qquad (2)$$

where:

m is the partition coefficient (Le Goff, 1979)

The obtained following equation shows that the C_e/C_0 ratio and, therefore, the removal is independent of the initial concentration, which was verified experimentally (Fig. 2):

$$\frac{C_e}{C_0} = \frac{1}{1+ m\rho} \qquad (3)$$

Different values of pH were obtained by using different volumes of HCl in the protonation step. The partition coefficient varied against pH according to a bell-shaped curve (Fig. 4). The sorption was maximum at pH between 3 and 5 and low beyond 6, a value close to the chitosan 6.2 pK_A (Muzzarelli, 1977). At pH lower than 2, the sorption was very weak as a probable result of the breakage of bonds between functional amino groups and glutaraldehyde. Moreover, the reaction involves the total bead volume, and not only its surface area. The sorption isotherms were indeed found to be identical with same volume of 1.5 and 4.5 mm diameter gel beads whose external surface areas are different (Fig. 4).

Some chemical considerations could explain the shape of the partition coefficient curve. Reticulated chitosan gel is an imine whose protonation can be described by (Roberts and Taylor, 1989):

$$RCH = NR' + H^+ \leftrightarrows RCH = N^+HR' \qquad (4)$$

where:

R and R' are carbonaceous cycles.

The acidity of the charged RCH = N$^+$HR' group was put into evidence by potentiometric titration. The titration of protonated cross-linked and non-cross-linked chitosan gels gave significantly different results (Fig. 5). The titration curve of the non-cross-linked gel has two inflexion points corresponding to the mixture of a strong acid (HCl) and a weak acid NH_3^+ that is a protonated amine (Kishimoto and Yoshida, 1995). On the other hand, the titration curve of cross-linked chitosan has only one transition point exactly like HCl. The RCH = N$^+$HR' group reacts with water in two steps (Roberts and Taylor, 1989); firstly with OH^-:

$$RCH = N^+HR' + OH^- \leftrightharpoons RCH(OH)\text{-}NHR' \qquad (5)$$

Then with H^+:

$$RCH(0H)\text{-}NHR' + H^+ \leftrightharpoons RCH(OH)\text{-}NH_2^+R' \qquad (6)$$

RCH(OH)-NH$_2^+$R' is a secondary ammonium group, which is particularly reactive and able to retain anions (Yoshida et al., 1994):

$$RCH(OH)\text{-}NH_2^+R' + NO_3^- \leftrightharpoons RC(OH)H\text{-}NH_2^+R', NO_3^-) \qquad (7)$$

Both Steps (5) and (6) are required for nitrate removal by Eq. (7) and an intermediate convenient pH value will maximise the partition coefficient.

The highest partition coefficients were obtained with distilled water (Fig. 3). The lower values, with tap water and groundwater, were probably due to competing ions. However, the partition coefficient was significantly higher for groundwater than for tap water, perhaps because of the chlorine content in the latter (Fig. 3). Chloride and sulphate did not modify the equilibrium but fluoride slightly lowered the nitrate sorption (Fig. 6). Considering the Lewis classification of bases and acids, the order from the weakest to the strongest is: Cl^-, F^-, SO_4^{2-} and NO_3^- (Bernard and Burnot, 1996). Hard acids react preferably and rapidly with soft bases while soft acids similarly react with soft bases (Jensen, 1980). Chloride is too weak to react; sulphate needs two close secondary ammonium groups, which reduces its effect. In spite of the fluoride interaction, the sorption capacity of nitrate remained significant.

Increasing pH to 12 with NaOH allowed desorption of nitrate without losing the effectiveness of the sorbent (Fig. 7). However, nitrate desorption and chitosan regeneration are not necessarily the best solution. Conventional ion exchange is indeed hampered by the production of high concentrated nitrate solution. Considering that chitosan is a soil conditioner that is able to prevent crop diseases (El Ghaouth et al., 1992), the best disposal should be the use of nitrated chitosan as a fertiliser that slowly liberates nitrate.

Sorption kinetics

The equilibrium was rapidly reached (Fig. 8). The removal rate r can be expressed by the following phenomenological equation (Le Goff, 1979):

$$r = -k(C - C^*) \qquad (8)$$

where k is an overall transfer coefficient and C* is the nitrate concentration in the liquid phase which would be in equilibrium with the adsorbed concentration q:

$$q = mC^* \qquad (9)$$

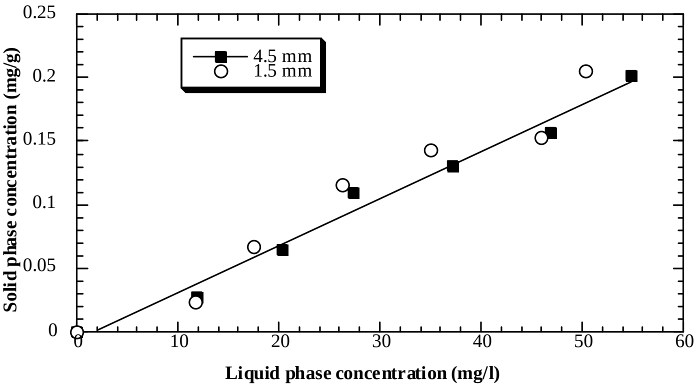

Figure 4
Equilibrium curve for 1.5 and 4.5 mm gel beads (distilled water, pH = 6.2)

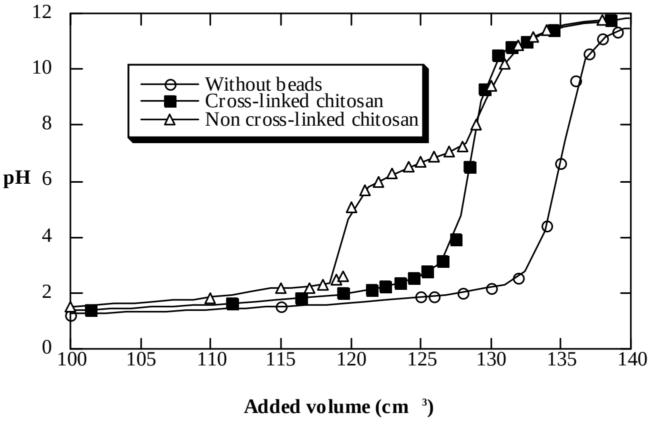

Figure 5
Potentiometric titration with 0.5 M NaOH

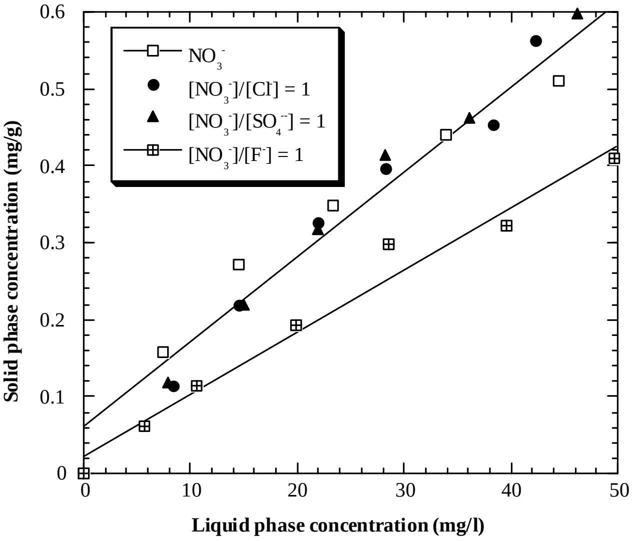

Figure 6
Equilibrium curve in presence of other ions (distilled water, pH = 5)

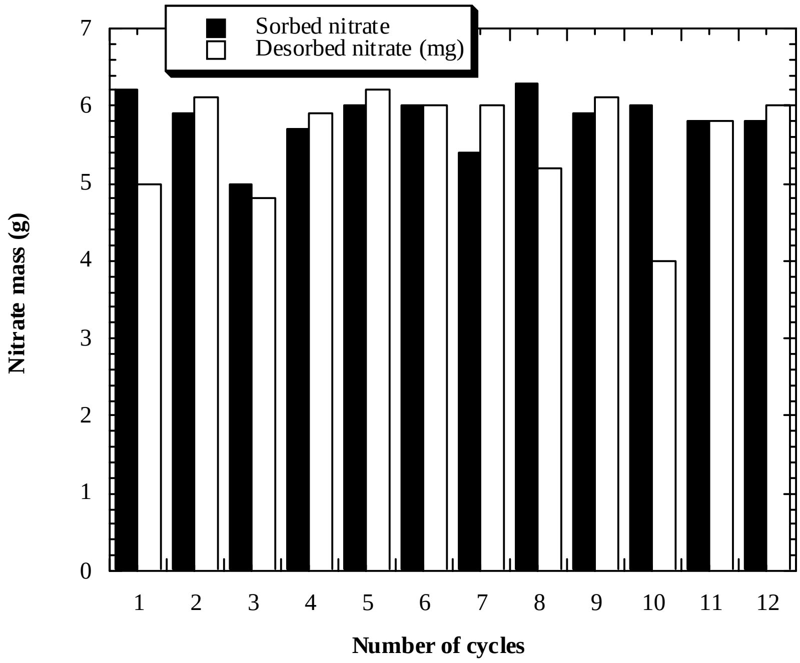

Figure 7
Sorbed and desorbed nitrate in 12 cycles (groundwater, sorption at pH 6.8)

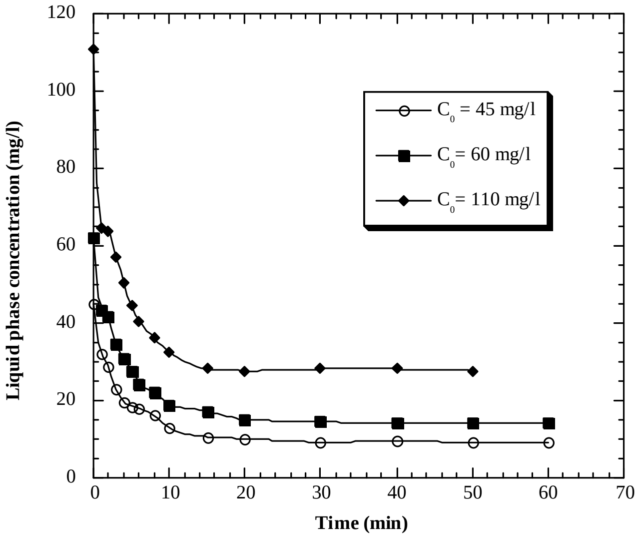

Figure 8
Liquid phase concentration against time (groundwater, sorption at pH 6.8)

m being the partition coefficient. Besides, the transient state mass balance is:

$$dq = -\frac{1}{\rho}\, dC \qquad (10)$$

By combining these equations and integrating, the transient concentration is obtained:

$$\frac{C}{C_0} = \frac{1}{1+m\rho} + e^{-kt} \qquad (11)$$

The model accuracy can be evaluated using the following equivalent equation, which should give a straight-line plot:

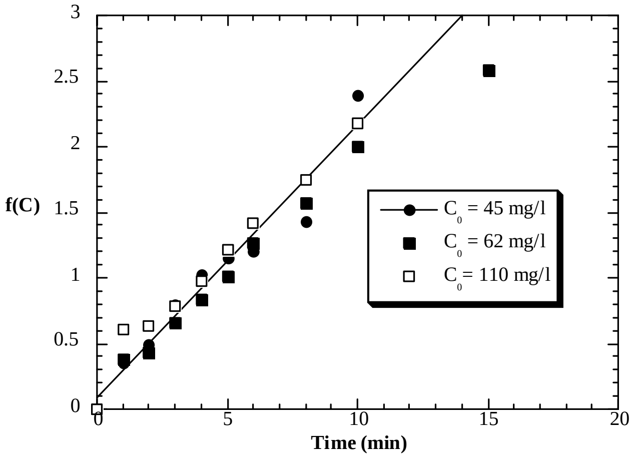

Figure 9
f(C) against time for different initial concentrations (groundwater, sorption at pH 6.8)

$$f(C) = \frac{1}{1+\alpha}\ln\left[(1+\alpha)\frac{C}{C_0} - \alpha\right] = kt \qquad (12)$$

with $\alpha = \frac{1}{m\rho}$

The plot of f(C) against time is indeed a straight line, which does not depend on the initial concentration (Fig. 9). The k value depended on pH and water quality, e. g. 0.2 min^{-1} at pH 3 and 0.04 min^{-1} at pH 7.3 for groundwater. Moreover the kinetics did not depend on the bead size (Fig. 10), which shows that pore diffusion does not limit the overall process. The mass transfer is not limiting either since the concentration depletion was identical at low and high stirring speed (Fig. 11). Such results could be the consequence of the high internal porosity of the gel beads, evaluated at 0.92 (Mitani et al., 1991).

Conclusions

- Protonated cross-linked chitosan gel can remove nitrate by a volume reaction.
- The sorption capacity depends on pH and is maximal at pH of between 3 and 5. However, the capacity is enough to remove nitrate from contaminated surface and groundwater without requiring a pH modification.
- The main process is probably an acid-base reaction involving amino groups.
- Fluoride is the main competitor. However, even in the presence of fluoride, the nitrate removal remains significant. Moreover, the fluoride sorption could open other applications to chitosan.
- The sorption capacity is recovered by increasing pH.
- Internal diffusion or mass transfer does not limit the sorption kinetics.
- The next step will be the design of a convenient reactor operated under real conditions.

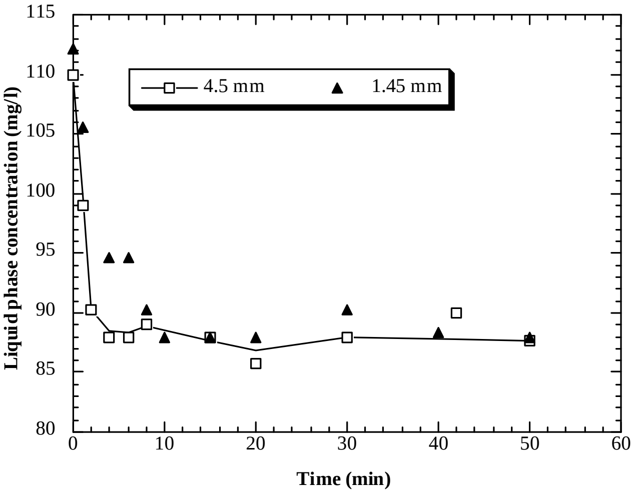

Figure 10
Liquid phase concentration against time for two different bead sizes (distilled water, sorption at pH 6)

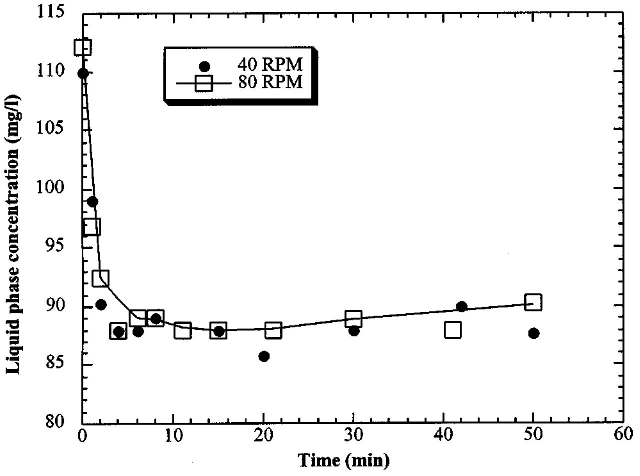

Figure 11
Liquid phase concentration against time for two different stirring speeds (distilled water, sorption at pH 6)

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