ARSENATE SORPTION ON MOLYBDATE -IMPREGNATED CHITOSAN GEL BEADS

Laurent DAMBIES, Eric GUIBAL, Angelina ROZE
Ecole des Mines d'Alès - Laboratoire Génie de l'Environnement Industriel
6, avenue de Clavières - F-30319 ALES cedex - FRANCE
Tel: +33 4 66 78 27 34 - Fax: +33 4 66 78 27 01 - email: ldambies@ensm-ales.fr

INTRODUCTION

Arsenic is an ubiquitous contaminant which can be found at high concentrations in natural waters and wastewaters. Arsenic containing wastestreams are generated mainly by the microelectronic industry and by pesticide and pharmaceutical facilities. As arsenic is a major hazardous contaminant for the human health, its removal is an issue of increasing concern. The removal technologies used are the coprecipation with ferric salts or adsorption onto activated carbon or alumina. However the drawbacks are respectively the generation of toxic sludges and the low adsorption capacity. Over the last three years, much research has been focused on the use of impregnated sorbents to improve arsenic removal.Activated carbon, minerals, synthetic resins as well as biopolymers are used in this goal. The objective of this study is to investigate a new adsorption process for the removal of As (V) ions from aqueous solutions using molybdate-based chitosan gel beads.

MATERIALS AND METHODS

Raw chitosan flakes were provided by Aber Technologies.
Reagents grade : Sodium arsenate $Na_2HAsO_4, 7H_20$.
Ammonium heptamolydate $(NH_4)_6Mo_7O_{24}, 4H_20$.
Orthophosphoric acid 84 %.
Metal salts : $Pb(NO_3)_2$, $FeCl_3$, $FeSO_4$, $Zn(SO_4)_2$, $Cu(SO_4)_2$, $MnSO_4$.
Anion salts : KNO_3, NaCl, K_2HPO_4.
pH control H_2SO_4 1 $mol.L^{-1}$ and NaOH 1 $mol.L^{-1}$.

PREPARATION OF THE SORBENT MICB
(Molybdate Impregnated Chitosan Beads)

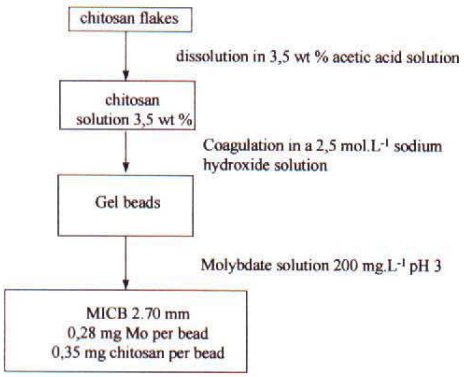

Figure n° 1: Preparation of MICB

EFFECT OF PH ON ARSENATE SORPTION ON MICB

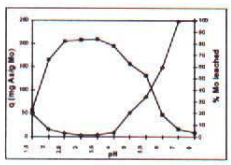

Figure n° 2: pH effect on arsenate sorption by MICB

- Arsenate sorption: pH dependant reaction
- pH range 2,5-4,0 : Best arsenate sorption
  Minimum molybdate leaching

MECHANISM OF SORPTION

Arsenate ions were adsorbed on the gel matrix by forming the well know arsenomolybdic complex. The active sites are then the molybdate ions and not amino groups of chitosan. The saturation of the sorbent leads to the formation of differents kinds of complex between arsenate and molybdate ions.
Molar ratio Mo/As vary from 8 to 4 depending on the sites coverage.

ISOTHERM SORPTION OF ARSENIC BY MICB

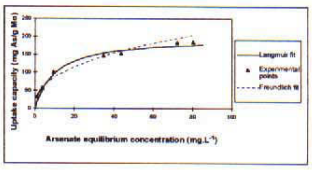

Figure n° 3: Isotherm sorption of arsenate ions on MICB pH 3

- Favorable isotherm curve.
- Langmuir fit r^2= 0,992
  qm= 197,6 mg/g Mo
  b= 0,1 $L.mg^{-1}$

EFFECT OF COMPETING IONS

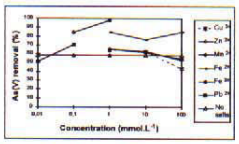

Figure n° 4: Influence of adding metal salts upon the adsorption efficiency of As (V).
20 MICB in 20 ml of As (V) solution (20 $mg.L^{-1}$)

- Fe^{2+}, Fe^{3+} and Pb^{2+} enhance adsorption by coprecipation.
- High concentrations of salts Cu^{2+}, Zn^{2+}, Mn^{2+} slightly affect arsenate sorption.

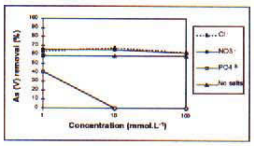

Figure n° 5: Influence of adding coexisting anions upon the adsorption efficiency of As (V).
20 MICB in 20 ml of As (V) solution (20 $mg.L^{-1}$)

- PO_4^{3-} greatly interferes with the adsorption due to the competition for active sites.
- High concentration of Cl^-, NO_3^- don't affect arsenate sorption.

ADSORPTION- DESORPTION STUDIES

Successful desorption is achieved with phosphate ions. During the desorption step, the phosphomolybdic complex is formed and takes the place of arsenate ions on the active sites.
pH has to be low to avoid molybdate leaching and phosphate concentration had to be high in order to shift the equilibrium.
For these reasons, a 0,1 $mol.L^{-1}$ orthophosphoric acid solution was chosen as the eluant.

	Adsorption 1	Desorption 1	Adsorption 2	Desorption 2	Adsorption 3	Desorption 3
Total arsenic sorbed (mg)	14,7	11,1	8,5	9,0	11,1	9,6
Molybdate released (%)	0,9	0,3	0,5	0,3	0,6	0,3

Table n°1: Adsorption- desorption cycles of As(V) by MICB on column system. Co As (V)= 153 ppm pH 3

- Complete regeneration of the sorbent with PO_4^{3-}
- Reuse of the sorbent for several adsorption-desorption cycles

CONCLUSION

Molybdate impregnated chitosan beads (MICB) were proved to be an effective sorbent for arsenic removal (fig.n°3). The sorption is selective to the arsenate ion and very specific. Desorption can be carried out with orthophosphoric acid and allows the sorbent to be used for several adsorption-desorption cycles (tab.n°1).
Further studies will focused on the stabilization of the resin and on the use of more impregnated beads in order to reduce the volume of sorbent.On a large scale, dynamic studies are under investigation with a pilot unit and has given very good results for the treatment of arsenate contaminated water.