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COPPER REMOVAL IN FIXED BEDS BY MODIFIED POLYACRYLONITRILE SORBENTS

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Abstract. Polyacrylonitrile (PAN) modified beads with carboxylic, amidooxime and amino groups called AMCAPAN were obtained. Column studies were performed with a.m. sorbents to determine the effect of flow rate, influent metal ion concentration and bed height on copper removal from aqueous solutions. The effect of co-ions Fe(II), Cd(II) and Cr(VI) over Cu(II) selectivity was examined. Kinetic considerations were carried out in order to identify the rate-limiting step. Regeneration studies by 1N H_2SO_4 and 0.5N EDTA were carried out varying eluants bed volumes and keeping flow rate constant. Number of regeneration cycles causing effective sorbents recovery was determined.

Keywords: adsorption, copper removal, polyacrylonitrile beads (PAN), regeneration.

AIMS AND BACKGROUND

The variety of production processes including metal processing, galvanizing, leaching, etc. lead to the formation of great quantities of wastewaters containing heavy metal ions. Waste waters treatment by the traditional reagent methods are not reliable enough with regards to heavy metal ions. The growing problem of heavy metal contamination has stimulated a search for new selective sorbents showing ion exchange and complexing properties towards heavy metals. Utilisation of chelate polymer sorbents capable of forming complexes with heavy metals allows a selective sorption to be carried out. Modification of polymer sorbents with the purpose of creating functional groups able to establish steady coordination with heavy metals have been carried out by many researchers[1-4].

Some modifications of acrylonitrile (AN) copolymers aiming to change some properties of the initial polymer have been reported in many research works[5-10].

Basically PAN fibers have been investigated for sorption of heavy metals from waste waters. Copper sorption by PAN fibers containing different amino, amidooxime and carboxylic groups have been analysed varying initial concentration, pH, and temperature of metal-bearing solution[11]. The application of mono-

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functional modified PAN with di-amido groups towards Cu(II), Zn(II), Co(II), Ni(II) has been revealed in Ref. 12 and the maximum uptake for Cu(II) has been determined. The possibilities for the utilisation of PAN filters for selective sorption of Cu(II), Zn(II), Co(II), Cd(II), Pb(II), Sn(II), etc. from metallurgical waste waters has been reported in Ref. 13.

The complexing properties of modified PAN sorbent which could be successfully used for the removal of heavy metal ions from natural water have been investigated in Ref. 14 and stability constant of complexes formed between copper, lead, zinc, cadmium, cobalt and nickel cations and the functional groups of the sorbent were determined.

Dynamic heavy metals removal from waste waters by polymer sorbents has been widely used by some researchers[15-18] and some kinetic parameters have been determined.

In our previous work[19] six types chemically modified PAN beads were analysed for Cu(II) and Pb(II) ions batch sorption uptake from aqueous solutions varying initial concentration of metal-bearing solution and pH. PAN sorbents modified with NaOH and NH_2OH called (AMCAPAN) were proved to be the best for metals uptake. Further experiments with AMCAPAN varying their porosity were carried out for Cu(II), Zn(II), Ni(II), Pb(II) sorption[20]. Best sorption properties were achieved for Cu(II).

The objective of this research was to investigate the effect of flow rate, influent metal concentration, co-ions availability and bed height on copper-ions dynamic removal from aqueous solutions by modified PAN granulated sorbents (AMCAPAN). The effectiveness of AMCAPAN regeneration was examined either.

EXPERIMENTAL

Materials and reagents. Polymer sorbents were obtained from acrylonitrile copolymer: acrylonitrile (AN90,6%), methylmethacrylate (MMA – 8.1%) and 2-acrylamidomethylpropensylphonic acid (AMPSA – 1.4%), product of Lukoil Neftochim, Bulgaria. Dimethylformamide, lithium nitrate and glycerin (Fluka Chemie AG, Switzerland) were also used for the preparation of polymer sorbents.

Modifications were carried out with sodium hydroxide and hydroxylamine (Fluka Chemie AG, Switzerland).

Solutions containing the desired concentration of Cu (II) were prepared by $CuSO_4.5H_2O$ (Fluka Chemie AG, Switzerland). Co-ion effect experiment was carried out by solution of $CdSO_4$; $FeSO_4(NH_4)SO_4.6H_2O$; $K_2Cr_2O_7$ (MERK Germany). 0.1N H_2SO_4 was used for pH adjustment. EDTA was used for determination of copper concentration in influent and effluent. Eluants used for desorption studies were 1N H_2SO_4 and 0.5N EDTA. All reagents were analytical grade.

Methods. Preparation and modifications of PAN sorbents. AN copolymer was dissolved in dimethylformamide till resultant solution of 9% was prepared. 1% $LiNO_3$ and 3% glycerin were added to the polymer solution. The mixture was pipetted dropwise into 20% aqueous dimethylformamide, whereby particles of porous structure were obtained.

Sorbents were swelled in 5 wt.% aqueous solution of dimethylformamide for 30 min at room temperature. Then they were immersed in a mixture (1:1) of 15 wt.% aqeous solution of NaOH and 15% aqueous solution of hydroxylamine for 50 min at 60°C. Polyampholites obtained were thoroughly washed with distilled water.

Metal uptake experiment. Fixed bed column runs were carried out using glass column (20 mm diameter) with a glass wool support. The column was conditioned by passing water acidified to the initial pH of the metal solutions. Weighted AMCAPAN sorbent with packed density 0.55 g/cm^3 was added to the column. The specific surface area and pore size of AMCAPAN were 19.9 m^2/g and 36.2Å, respectively. The particles size of the sorbent was 0.5 mm. Copper bearing solutions with various flow rates (u=0.5-2.5cm^3/min), and initial concentration 0.5-2.5 g/dm^3 run under gravity through the sorbent. Column runs were observed till full exhaustion of the sorbent was achieved (metal ion concentration in the influent and effluent solutions became equal). The amount of copper ions was measured in effluent equal volumes. Dynamic sorption uptake was determined at different flow rates and bed heights (H) of AMCAPAN when 100% of the sorbents capacity was consumed and calculated by equation:

$$DU = \frac{(C_1 - C_2)V}{G} \quad , \quad \text{mg eq/g}$$

where DU is dynamic sorption uptake of the sorbent, mg eq/g ; C_1 and C_2 – initial metal ions concentration in influent and effluent respectively, mgeq/cm^3; V – effluent volume, cm^3; G – dry resin weight, g.

Kinetic considerations. The sorption of copper on AMCAPAN at different flow rates and bed heights as a function of time was determined. Such data are plotted as degree of sorption (degree of conversion of the active functional groups) F and -ln(1 – F) versus time, where:

$$F = Q_t / Q_\infty$$

where Q_t is the dynamic sorption uptake at time t, mg eq/g and Q_∞ dynamic sorption uptake at sorbents full exhaustion, mg eq/g. These data are necessary to determine the rate-limiting process-external(film)diffusion characterised by the equation: $-\ln(1-F)=\beta' t$ or intraparticle diffusion characterised by equation: $F=\beta t$ where β and β' are constants.

Regeneration studies. Recovery of copper adsorbed on the column was performed under dynamic conditions by elution with known volumes of 1N H_2SO_4 and 0.5N EDTA keeping constant flow rate (0.5 cm^3/min). Sorption capacity for the regenerated sorbents was accessed and desorption was expressed as a percentage of the sorbents initial loading. The number of regeneration cycles under which recovery of sorbents decreases to 50% were determined varying eluants bed volumes (BVs)(1BV-4BVs).

Apparatus. Copper and co-ions concentration in metal bearing solutions were checked by MERK spectrophotometer SQ118. Specific surface area, pore volume and pore radius of AN copolymer were determined on a Autosort-3B, Quantachrome Corporation, USA.

RESULTS AND DISCUSSION

In the present paper adsorption studies were conducted with copper ions in aqueous solutions in fixed beds using modified PAN beads. The polymer beads were obtained and modified by a method described in the Experimental section and revealed in our previous paper[20]. Above mentioned sorbents with introduced carboxylic, amidooxime and amido groups were called AMCAPAN and recommended by our staff as sorbents with highest amount of functional groups, stable mechanical structure and highest heavy metal uptake (especially for Cu) under static conditions and pH value 3.5.

Fixed bed column runs were carried out by passing copper-bearing solutions through the sorbents. The effect of flow rate on copper removal was illustrated by varying flow rate (0.5; 1.5; 2.5 cm^3/min) and keeping initial copper concentration 2 g/dm^3, sorbents height 3cm and pH 3.5. The copper concentration profile in effluent as a function of influent volume is shown in Fig. 1. It is obvious that lower flow rate resulted in more copper ions removed by AMCAPAN sorbent especially for the first influent volumes (up to 60 cm^3). The variety of flow rates lead to sorbents full exhaustion at different influent volumes. The lower the flow rate the greater the volume at which 100% of sorbents capacity was consumed. As the flow rate of the metal bearing solution was decreased, the contact and retention time of the column was increased resulting in more copper ions removed. With the increasing of flow rate, the boundary layer thickness decreases, decreasing film resistance. The mass of adsorbed copper per gram sorbent at complete exhaustion (G_{exh}), dynamic sorption uptake (DU) and volume of influent at sorbents complete exhaustion (V_{exh}) at different flow rates are presented in Table 1. The highest uptake achieved was 1.40 mg eq/g for 0.5 cm^3/min flow rate.

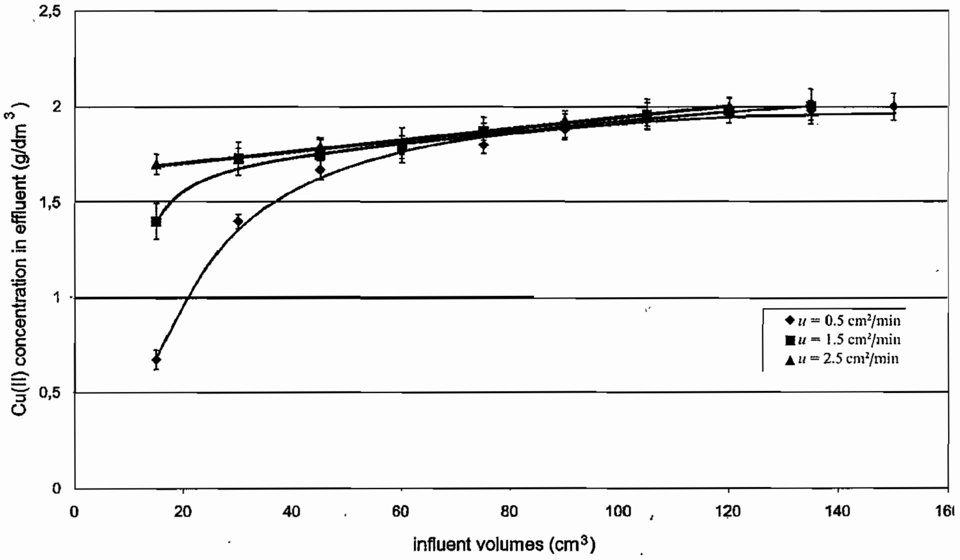

Fig. 1. Influence of influent flow rates on Cu(II) sorption by AMCAPAN: C_{0Cu} =2 g/dm^3, pH=3.5

Table 1. Fixed bed performance of AMCAPAN for Cu removal at different flow rates

U (cm^3/min)	V_{exh} (cm^3)	G_{exh} (mg/g)	DU (mg eq/g)
0.5	150	44.25	1.40
1.5	135	24.10	0.78
2.5	120	18.25	0.57

Effect of initial copper concentration in influent on AMCAPAN sorption capacity was established (see Fig. 2). Column experiments were conducted at 2.5; 2.0; 1.0; 0.5; 0.2; 0.1 and 0.05 g/dm^3 copper influent concentrations keeping flow rate 0.5 cm^3/min, sorbent height 3 cm and solution pH 3.5. The increase of the initial concentration increased copper dynamic uptake to 1.4 mg eq/g. The decrease in Cu(II) uptake at lower initial concentrations could be a result of metal hydrolysis in water which hinder the sorption process.

The effect of co-ions Fe(II), Cr(VI) and Cd(II), available in most cases in metallurgical effluents, on Cu(II) uptake was examined. Analysis were carried out varying co-ions initial concentration, keeping copper influent concentration constant (2 g/dm^3) and pH 3.5. In all cases copper uptake was depressed insignificantly when increasing co-ions concentration (Fig.3). Most depressive for Cu(II) dynamic sorption was Cd(II) interference while Fe(II) had negligible effect even at higher levels of concentration.

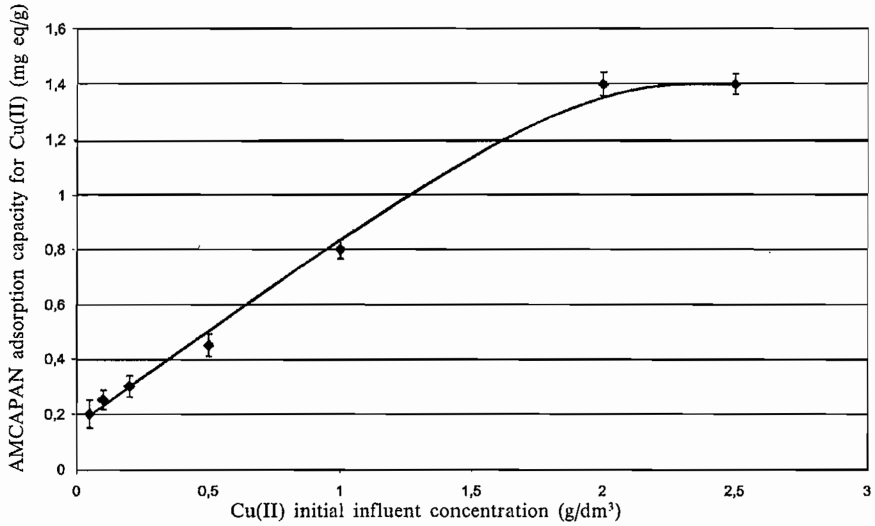

Fig. 2. Influence of copper initial concentration on AMCAPAN sorption capacity, u=0.5 cm^3/min, pH=3.5

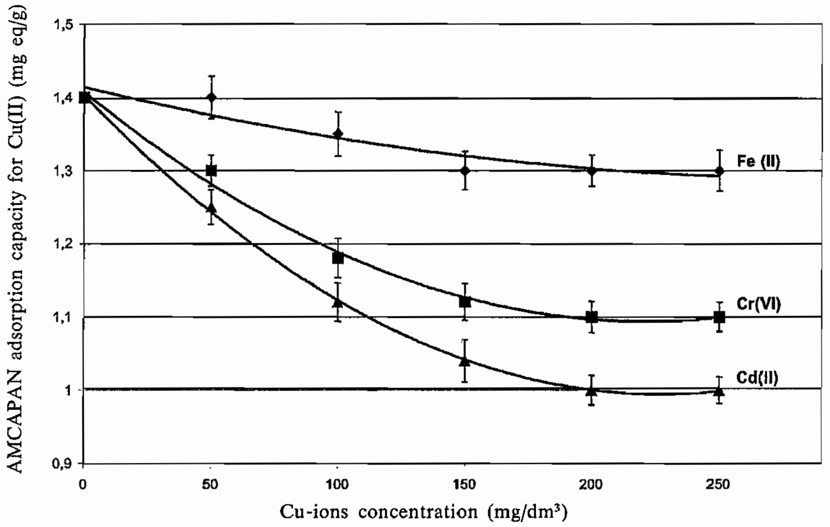

Fig. 3. Co-ions effect on Cu(II) sorption by AMCAPAN: C_{0Cu}=2 g/dm^3, u=0.5 cm^3/min, pH=3.5

Some authors explained heavy metals selectivity with their different stability constant[21]. The main reasons for the negligible effect of co-ions over Cu(II) selectivity might be pH value of metal-bearing solution which is optimal for copper sorption but not for the co-ions as well as the higher stability of the complexes formed by copper. The determined order of selectivity is similar to Ashirov and Williams[21,22] established series for the stability of transition metal complexes with some ampholites. The reduced sorption of Fe(II) is explained by some researchers with its more stable hydrating than chelating complexes[23].

The effect of sorbents bed height on the removal of copper ions was determined either and illustrated in Fig.4. The experiments were carried out with flow rate 0.5 cm^3/min, initial copper concentration 2 g/dm^3, pH 3.5 and bed heights from 3 to 11 cm. The volume required for sorbents complete exhaustion (V_{exh}) was increased with the increase in sorbents height. The effectiveness of copper removal was reduced significantly in the last effluent volumes when complete sorbents exhaustion was reached. Effluent volumes at breakthrough increase with the increase in bed height which normally is connected with the increase in column retention. The mass of adsorbed copper per gram sorbent at complete exhaustion (G_{exh}), AMCAPAN dynamic uptake (DU) and some of the above mentioned parameters at different bed heights are presented in Table 2. The sorbents capacity reached 2.00 mgeq/g for 11 cm bed height.

Table 2. Fixed bed performance of AMCAPAN for Cu removal at different bed heights

H (cm)	V_{exh} (cm^3)	G_{exh} (mg/g)	DU (mg eq/g)
3	150	44.25	1.40
5	210	55.70	1.75
8	285	60.00	1.89
11	360	63.85	2.00

The sorption of metal ions involves mass transfer accompanied by chemical reaction. The chemical reaction at the sorption sites in the resin is usually too

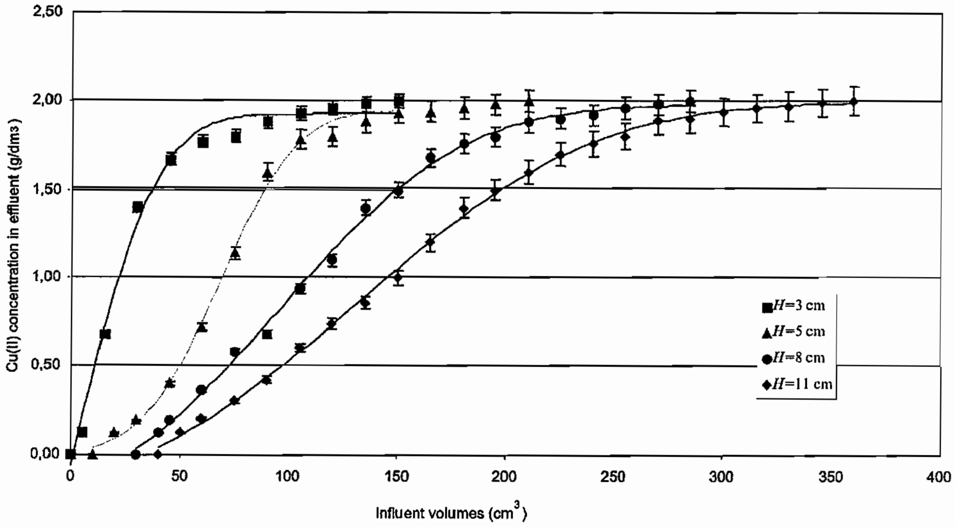

Fig. 4. Influence of bed height on Cu(II) sorption by AMCAPA: C_{0Cu}=2 g/dm^3, u=0.5 cm^3/min, pH=3.5

fast to affect the overall sorption rate. The rate-limiting step in most cases has been established to be either intraparticle diffusion or external film diffusion. In order to determine what kind of mass transfer controlled Cu(II) sorption and since relatively few sorption data were available simple model was used. Sorption of Cu(II) as a function of time was measured, the degree of sorption(degree of conversion of the active functional groups) F and -ln(1-F) were calculated for equal time periods till complete sorbents exhaustion and plotted versus time (Figs 5 and 6).

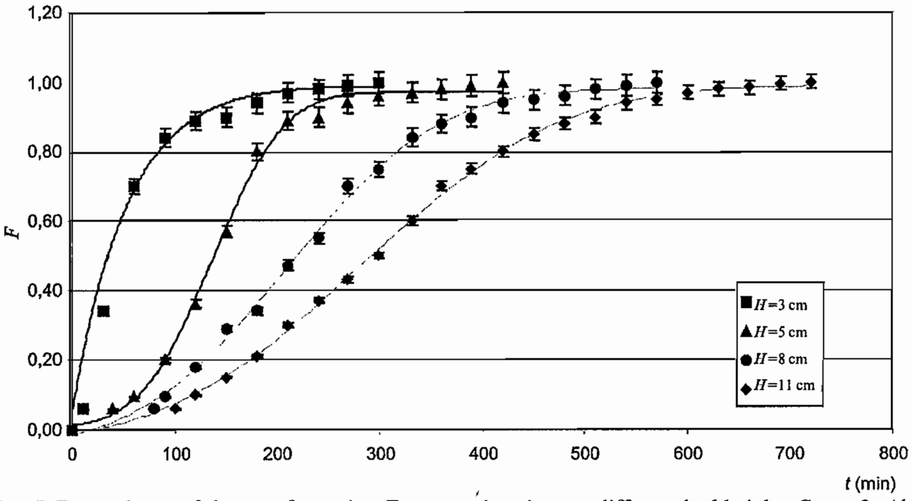

Fig. 5. Dependence of degree of sorption F on sorption time, at different bed height; C_{0Cu} = 2 g/dm^3, pH=3.5, u=0.5 cm^3/min

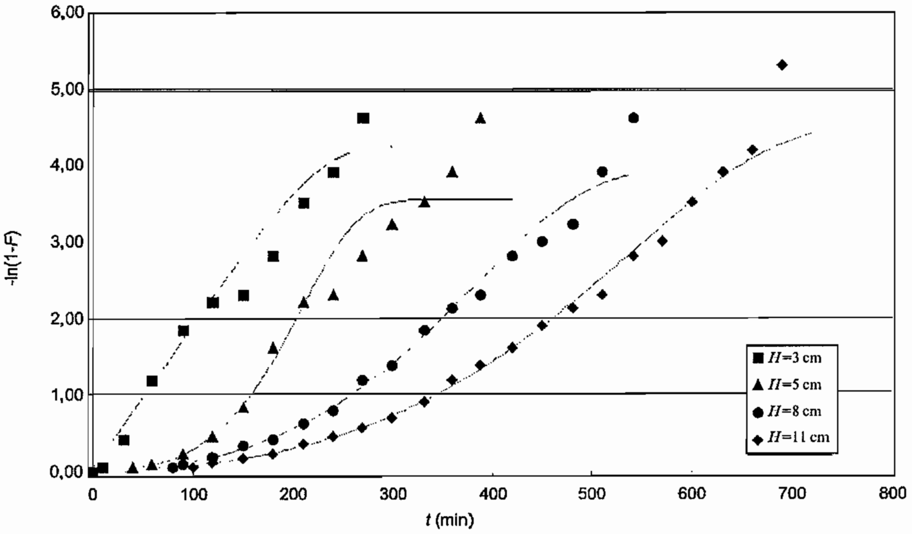

Fig. 6. Dependence of -ln(1-F) on sorption time at different bed height: C_{0Cu}=2 g/dm^3, pH=3.5, u=0.5 cm^3/min

The kinetic curve concerning 3-cm bed height (Fig. 5) exhibits intraparticle diffusion controlling the sorption. The initial segment of this curve to $F = 0.4$-0.6 could be accepted as linear. Quite different is the case with the other three curves concerning bed height – 5, 8, 11 cm. They have approximately "S" shape which means that the sorption process was not under intraparticle diffusion. Having in mind the a.m. and the fact that the plots on Fig. 6 (characterising external diffusion model) are not linear either, a conclusion could be made that sorption for 5.8 and 11 cm, height was controlled not only by external film or intraparticle diffusion but by both processes, i.e. by heterogeneous diffusion. The initial segments of the S-shaped curves on Fig. 5 (H = 5, 8, 11 cm) are not linear which means that external film diffusion is the rate-limiting step at the beginning of copper uptake. This could be explained with the increase in bed resistance. At the end of the process when AMCAPAN complete exhaustion was reached sorption should be under the control of the intraparticle diffusion because a great part of the functional groups were occupied and the access of the heavy metal ions to the unoccupied ones would be more difficult. The increase in sorbents bed height affects the diffusion of copper ions to the surface of the beads causing increase in the time required for complete exhaustion of the sorbent. After 80% saturation of the active groups the uptake became rather inefficient.

Important property of sorbents is their regeneration and re-use after their partial or complete exhaustion.Our previous studies[24] show that effective regen-

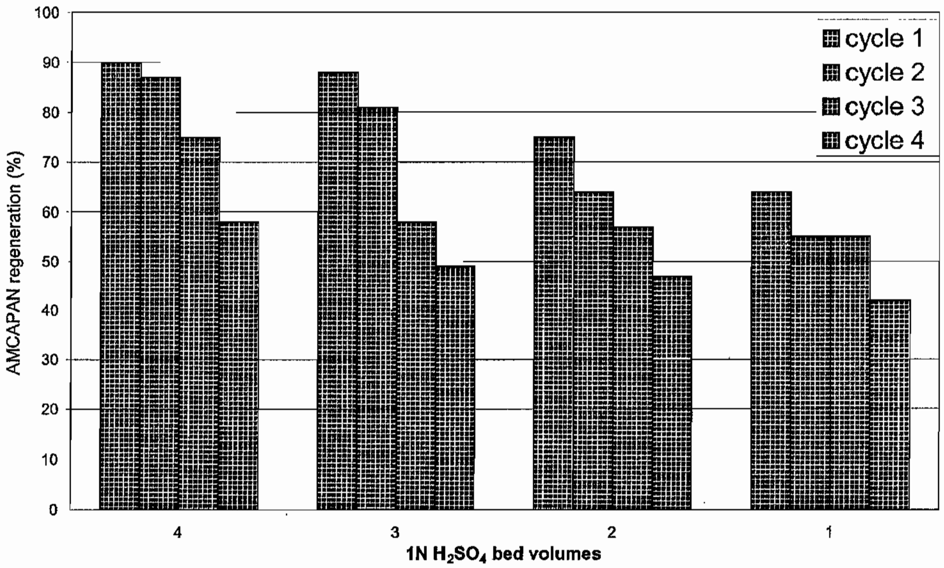

Fig. 7. AMCAPAN regeneration effect after several elution cycles by different bed volumes of 1N H_2SO_4; u=0.5 cm³/min

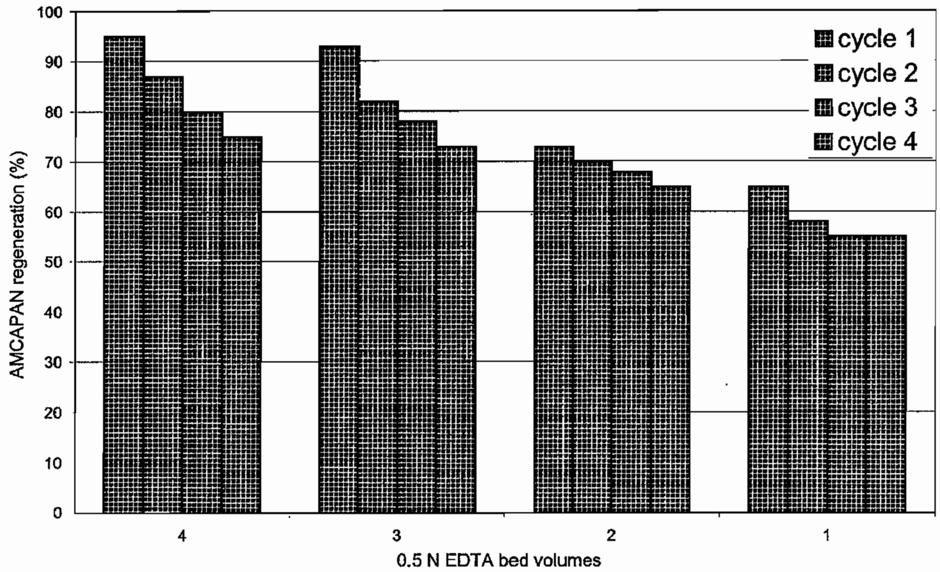

Fig. 8. AMCAPAN regeneration effect after several elution cycles by different bed volumes of 0.5N EDTA; u=0.5 cm^3/min

eration of AMCAPAN could be achieved by two eluants – 1N H_2SO_4 and 0.5 N EDTA. In this connection eluation under dynamic conditions with a.m. regeneration agents through 11-cm bed height column was performed. Eluants volumes were varied from 1BV – 4BVs, keeping flow rate – 0.5 cm^3/min. Regeneration cycles with different bed volumes of eluants were carried out till sorbents effectiveness decreased under 50%. Each cycle includes: sorption-regeneration-rinsing with distilled water and sorption again.The effect of regeneration after each cycle for H_2SO_4 and EDTA different BVs was calculated (see Figs 7 and 8). Almost complete desorption of Cu(II) was observed after first cycle at 4 BVs of the eluants. AMCAPAN sorbents were effective enough even after the fourth cycle. Both regenerating agents were competitive enough but sulphuric acid showed a little bit lower regeneration properties. After the fourth cycle sorbent recovery was decreased significantly especially when 2BVs or 1BV of H_2SO_4 were used. Nevertheless, sulphuric acid is preferred for copper eluation because further electrochemical recovery could be applied.

Kinetics of copper recovery was investigated by passing 1N H_2SO_4 through AMCAPAN – 11-cm bed height and 0.5 cm^3/min. Copper concentration was determined at constant intervals showing that 80 min were enough for almost complete metal ion removal.

CONCLUSIONS

AMCAPAN efficiency was determined for Cu (II) removal from aqueous solutions under dynamic conditions. The influence of flow rate, metal initial concentration and bed height on copper removal was established. The highest uptake achieved was 2 mg eq/g at flow rate 0.5 cm^3/min, bed height 11 cm and pH 3.5. The effect of co-ions Fe(II),Cd(II) and Cr(VI) over Cu(II) selectivity was examined. In all cases copper uptake was depressed insignificantly. Kinetic considerations were carried out in order to identify the rate-limiting step. In most cases kinetic of sorption was determined to be heterogeneous – neither external nor intraparticle diffusion controlled the process only. Regeneration was performed successfully by 4BV of 1N H_2SO_4 and 0.5 N EDTA. The number of the effective regeneration cycles was determined – 4 BVs.

AMCAPAN was found to quantitively remove copper from aqueous solutions and could be used for efficient sorption of heavy metals from contaminated waters.

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