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Copper Sorption from Aqueous Solutions by Plasma Modified Polyacrylonitrile Beads

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Abstract

The adsorption of Cu (II) ions from aqueous solutions on acrylonitrile(AN) copolymer sorbents has been studied. Porous sorbents from acrylonitrile copolymer- 90,6% acrylonitrile (AN), 8,1% methylmethacrylate (MMA) and 1,4% 2-acrylamido-methylpropensylfonic acid (AMPSA) have been prepared and modified by ammonia, air and ethylenediamine plasma. Fourteen types of sorbents have been obtained changing plasma agent and plasma vacuum. The Cu (II) ions uptake has been studied and the sorbent with best sorption characteristics determined. The best sorption uptake has been achieved for the modified sorbent obtained at ethylenediamine plasma modification under 5Pa plasma vacuum (PAN1-1,20 mgeq/g). Effect of sorbents regeneration after different elution cycles has also been investigated . The sorbents showed high effectiveness of regeneration towards Cu (II) ions, which was above 50% after the IV cycle of elution.

Keywords:

copper ions, sorption, acrylonitrile copolymer, plasma modification, regeneration

Introduction

Water pollution due to toxic heavy metals remains a serious environmental and public problem. Copper, one of the most widely used heavy metal is mainly employed in many industries such as electrical and electroplating processes. In large amounts it is extremely harmful for living organisms and is of serious toxicological concern.
One of the treatment processes for copper removal from contaminated waste waters includes adsorption methods. Wide variety of sorbents- natural, synthetic and biosorbents are used for that purpose.

Chitin due to its abundance in nature found in the exoskeletons of crabs and other arthropods and in the cell walls of some fungi was used for heavy metals adsorption [1]. Some methods for conversion of chitin to chitosan were used to investigate copper removal efficiency and the rates of adsorption to be compared [2-3].

Strong candidates for heavy metals removal are natural materials as bentonite, zeolite, perlite etc. Their abundance in nature and low cost make them competitive and useful adsorbent for copper ions uptake [4-6].

Removal or copper ions by synthetic polymer materials is another widely used method. In Sevil Veli and Beyhan Pekey [7] work ion exchange resin was handled for the purpose of copper removal. Strong cationic Dowex HCR and Dowex Marathon C resins were chosen. Theoretical and experimental investigations for copper removal by chelating resins were revealed in Shen Lin's work [8].

In order to increase sorption capacity of polymer sorbents, different surface modifications were carried out. Treatment with plasma is comparatively new method for polymer surface modification .Due to the polymer surface permeability towards plasma action this method is very suitable for modification and generation of surface functional groups. With plasma treatment, it is possible in a well-controlled reproducible way to activate, etch or modify the polymer surface without changing in most of the cases material structure and porosity.

By introducing inorganic or organic gases and monomers into the electrical discharge, specific functional groups can be applied into the polymer. Kristen [9] established the incorporation of NH_X and OH species in the polyethersulfone membrane (PES). Nitrogen- based plasma system as N_2, NH_3, Ar/ NH_3 and O_2/NH_3 were used to modify this membrane. The success of amino functional groups grafting on polypropylene microporous membrane was demonstrated by Tang J. [10]. Nitrogen and hydrogen (1:2) plasma mixture was used for treatment of this membrane. The interaction of a polyurethane with air plasma was carried out to increase C=O and C=C at the surface [11]. Presence of new functional groups such as ketons, aldehydes and imines were also indicated .

With plasma treatment, it is possible to achieve better transport characteristics of polymer membranes. Enhanced surface hydrophilicity of polyvinyl chloride membrane was observed, after nitrogen or oxygen plasma treatment of the membrane[12]. The effect of oxygen plasma on the surface hydrophilicity of polyurethane membrane was studied also by Yesim[13].

The influence of the main operating parameters, i.e. plasma power, treatment period duration, electrodes gap, modifying agent concentration and type, on the surface properties was studied by Chaozong L.[14], Yang S.[15] and Alina [16]. Kenzie D. et al**.** [17] found out that hydrogen treatment produced the deepest modification compared with oxygen and argon plasma. It is well know that polyacrylonitrile (PAN) doesn't possess reactive groups and they could be created by special modifications. There are a lot of papers about chemical treatment of PAN by different modifying agents [18-23]. In our previous investigations [24-26] porous PAN beads were prepared and chemicaly modified in order to create functional groups able to make complexes with heavy metal ions from aqueous solutions. These sorbents exhibit high sorption uptake towards heavy metal ions.

The aim of this study was to prepare plasma modified PAN beads and to study their batch adsorption related to copper ions from aqueous solutions.

Experimental

Materials

Polymer sorbents were obtained from AN copolymer: acrylonitrile (AN) -90,6%, methylmethacrylate (MMA) -8,1% and 2-acrylamido-methylpropensylfonic acid (AMPSA) - 1,4%(product of Lukoil Co, Bourgas, Bulgaria). Dimethylformamide(DMF), lithium nitrate and 1,2,3-trihydroxypropane(Fluka Chemie AG, Buchs, Switzerland) were also used for the preparation of polymer sorbents.
Model solutions with certain concentrations of copper metal ions were prepared from $CuSO_4.5H_2O$ (Fluka Chemie AG, Buchs, Switzerland). All reagents were analytical grade.

Preparation of porous sorbents from AN Copolymer

Acrylonitrile copolymer 9 g or 18 g was dissolved in 100 ml DMF and homogenized in water bath at 60°C under continuous stirring. Then, 1g $LiNO_3$ and 3g 1,2,3-trihydroxypropane were added to the polymer solution. The mixture was pipetted into 20 wt% aqueous DMF coagulation bath, whereby beads of porous structure were obtained. All granules obtained were washed thoroughly with distilled water and then kept in 30% solution of 1,2,3-trihydroxypropane for 3 h. Finally, the granules were dried at 60°C to constant weight.

Plasma modification of AN copolymer beads

Air, ammonia and ethylenediamine were used as modification agents. Plasma treatment was carried out under the following conditions-el. current 1-1,4A; voltage-380V; frequency 6-10kHz; vacuum 1-100Pa; treatment time-10min.; temperature-293K; quantity of modification agent used 5-6cm^3.

Adsorption and desorption studies

The adsorption experiments were performed on a rotating shaker. AN copolymer sorbent (1g) was immersed in 50 cm^3 copper-bearing solution with concentration 2,0g/dm^3 and stirred at 400rpm, 20°C and pH 3 . Samples at 10 min. intervals ware taken and analyzed for Cu(II) ions by complexometric titration until equilibrium was reached. The metal uptake (adsorption capacity) was calculated by the following equation:

$$a = \frac{(C_0 - C_f)V}{1000.m}, [\text{mg/g}]$$

where:
V - volume of the solution in the contact batch flask(ml),
C_0 - initial concentration of the metal ions, mg/l,
C_f - equilibrium concentration, mg/l,
m - weight of the sorbent, g.
Desorption of the heavy metals was carried out by 1N H_2SO_4 for 60min. under static conditions. The regenerated granules were used for the next sorption cycle. Effectiveness of desorption was determined according to adsorption uptake of fresh sorbents and regenerated ones and was expressed in percent: $(a_1/a_n).100$, were a_1-adsorption uptake of the fresh sorbent; a_n –adsorption uptake of the regenerated sorbent.

Results and discussions

This study examined Cu (II) batch sorption from aqueous solutions by plasma modified AN copolymer beads. AN copolymers of 9% or 18% were used for the preparation of polymer beads because in our previous investigations these concentrations were optimum for obtaining sorbents with best surface characteristics and sorption uptake related to heavy metal ions [24,25,26]. The specific area and pore volume of beads from 9% AN copolymer were-19,9 m^2/g and 0,019cm^3/g and from 18% AN copolymer - 7,61m^2/g and 0,013cm^3/g. All granules obtained were spherical and of approximately the same size (0,5mm). They were modified by ethylenediamine, ammonia and air plasma. Plasma modification conditions were: 1-1,4A/6-10kHz el.current; modification agent 5-6cm^3; modification time-10min, vacuum-1, 5, 15, 30, 60, 100 Pa.

Table 1 AN copolymer beads characteristics

Type of AN copolymer sorbents	Concentr. of AN copolymer,%	Plasma modification agent	Plasma vacuum, Pa
PAN 1	9	Ethylenediamine*	5
PAN 2	9	Ethylenediamine*	15
PAN 3	9	ethylenediamine*	30
PAN 4	9	ethylenediamine*	60
PAN 5	9	ethylenediamine*	100
PAN 6	9	ammonia**	1
PAN 7	9	ammonia**	15
PAN 8	9	ammonia**	30
PAN 9	9	ammonia**	60
PAN 10	9	ammonia**	100
PAN 11	9	ammonia**	5
PAN 12	9	air***	5
PAN 13	18	ammonia**	5
PAN 14	18	air***	5

The aim of plasma modification was introduction of amino and oxygen-containing functional groups in bead surface under soft conditions. The amino groups were introduced in polymer surface after ethylenediamine and ammonia plasma modification and the oxygen containing functional groups after air plasma modification. Cold plasma (293K) was used due to the low heat resistance of the polymer beads. Plasma modification was carried out changing some parameters in order to obtain sorbents with best sorption uptake (capacity). In this connection 14 different types of sorbents were formed and presented in table 1.

The amount of amino and oxygen groups in all modified sorbents was determined analytically. Amino groups content is presented in table 2. The highest amount of amino groups was reached by using ethylenediamine as plasma agent for modification. PAN1 is the sorbent with the highest amount of amino groups - 0,94mgeq/g. Most of the sorbents show reduction of amino groups with the increasing of vacuum during plasma action.

Table 2 Amino groups content(mgeq/g) in AN copolymer sorbents modified by ethylenediamine*and ammonia** plasma

Sorbents	aminogroups	Sorbents	aminogroups	Sorbents	aminogroups
PAN 1*	0.94	PAN 6**	0.58	PAN11**	0.60
PAN 2*	0.86	PAN 7**	0.54	PAN13**	0.50
PAN 3*	0.86	PAN 8**	0.54		
PAN 4*	0.74	PAN 9**	0.48		
PAN 5*	0.70	PAN 10**	0.40		

The amount of oxygen groups in PAN 12*** and PAN 14*** treated with air plasma*** is 0,65 mgeq/g and 0,44 mgeq/g respectively.

Nitrogen containing functional groups are with proven complex forming properties related to heavy metal ions. Batch sorption with the above-mentioned 14 sorbents was carried out related to copper ions, because according our previous experiments with chemically modified PAN sorbents highest uptake concerning Cu (II) ions was achieved [25].

Adsorption kinetics were investigated and presented in fig.1-3. All sorbents showed high copper sorption rate. Complete saturation was reached for about 30 min. Maximum copper uptake(adsorption capacity) regarding all types of sorbents is presented in table 3.Considerable highest uptake exhibited sorbents treated with ethylenediamine plasma. PAN sorbents from 9%AN copolymer treated under low plasma vacuum (1-5 Pa) reached highest uptake. With the increase of plasma vacuum copper ions uptake decreased.

When plasma vacuum is varied two typical fields of plasma modification are formed-field of high frequency discharge (< 40 Pa) and field of normal discharge. It was established [27] that the surface modification of sorbents was considerable under vacuum less than 40 Pa (especially under 10Pa). Having in mind the above we can suggest that under low vacuum high degree of modification can be achieved which leads to formation of great amount of functional groups and higher sorption uptake.

Table 3 Cu (II) sorption uptake (mgeq/g) of AN copolymer sorbents modified with ethylenediamine*, ammonia** and air*** plasma

Sorbents	Sorption uptake	Sorbents	Sorption uptake	Sorbents	Sorption uptake
PAN 1*	1.20	PAN 6**	0.96	PAN11**	0.98
PAN 2*	0.79	PAN 7**	0.55	PAN12***	1.00
PAN 3*	0.79	PAN 8**	0.50	PAN13**	0.72
PAN 4*	0.66	PAN 9**	0.36	PAN14***	0.65
PAN 5*	0.62	PAN 10**	0.30	--	--

PAN1 modified with ethylenediamine reached highest uptake 1,20 mgeq/g, followed by PAN12 and PAN11. PAN 11 sorbent was modified with ammonia and PAN 12 with air plasma. PAN 1, PAN 11 and PAN 12 were modified under low vacuum of the plasma-5Pa, which means that this factor was determinative. A conclusion can be made that the most important factor for the highest sorption uptake is plasma vacuum. In our case the type of the modifying agent doesn't play an essential role.

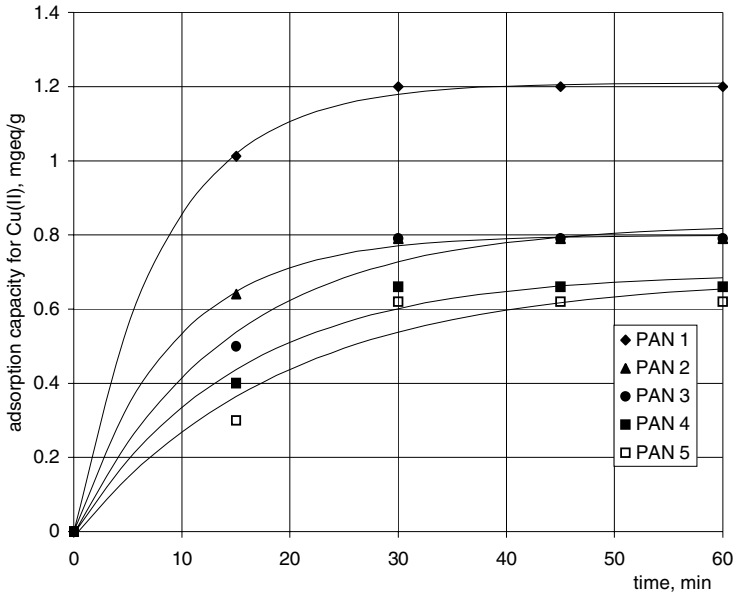

Figure 1 Kinetics of sorption of Cu (II) on plasma modified PAN1, PAN2, PAN3, PAN4 and PAN5 sorbents

PAN13 and PAN14 sorbents which were products of ammonia and air treatment of 18% AN copolymer beads under 5Pa vacuum exhibited sorption uptake related to Cu (II) ions less than PAN 11 and PAN 12 (9% AN copolymer). The reason for these results is probably the better surface characteristics of 9% AN copolymer beads than the 18% AN copolymer beads. Comparing the sorption uptake of PAN 13 (from 18 % AN copolymer) with that of PAN 7-10 sorbents (from 9% AN copolymer), all

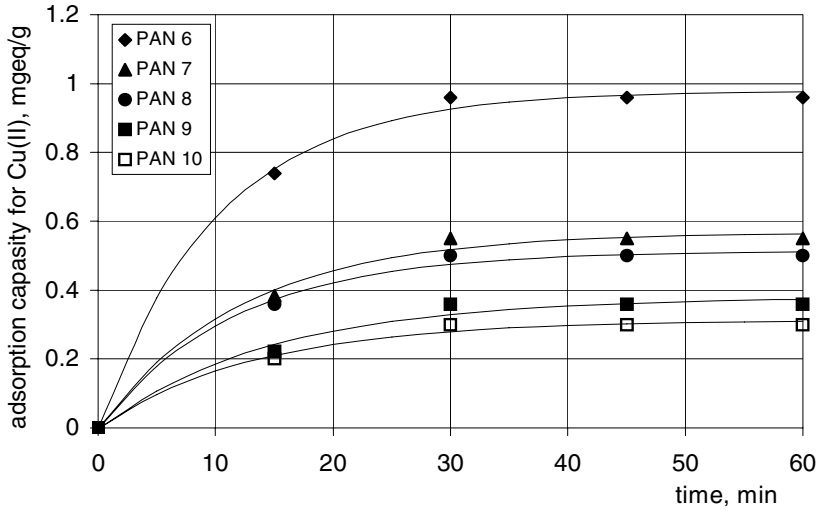

Figure 2 Kinetics of sorption of Cu (II) on plasma modified PAN6, PAN7, PAN8, PAN9 and PAN10 sorbents

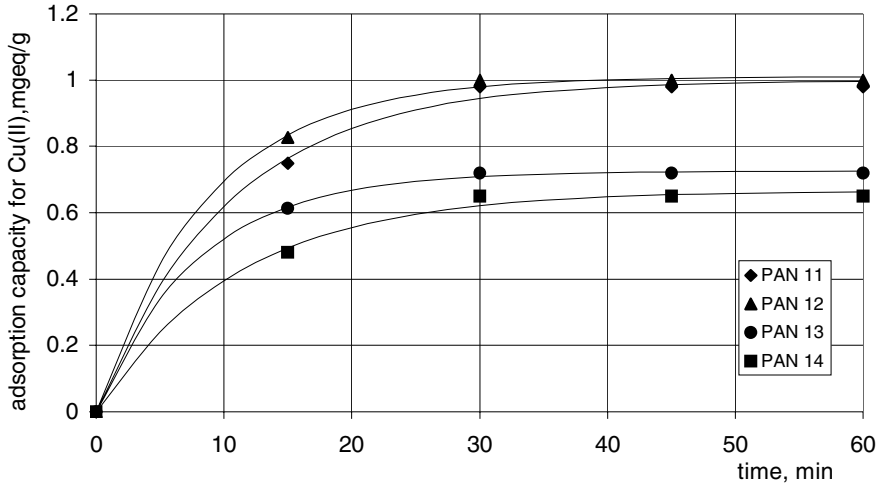

Figure 3 Kinetics of sorption of Cu (II) on plasma modified PAN11, PAN12, PAN13, PAN14 sorbents

modified with ammonia plasma, a considerable higher uptake for PAN 13 was reached (0,72mgeq/g). This means that AN copolymer concentration was not determinative and confirms once again our conclusion that the most important factor for the highest metal ion uptake is plasma vacuum.

The effect of ethylenediamine, ammonia and air plasma modification upon regeneration of PAN1, PAN11 and PAN12 was investigated. Elution for 60 min. under static conditions was carried out using 1N H_2SO_4 . A number of cycles sorption-elution was carried out and sorption uptake was determined. Regeneration cycles were repeated till 50% recovery of the sorbents(fig4). The best regeneration was reached for PAN12, which was above 90% after the first elution and about 60% after the IV cycle. This could be explained with the weak complexes, which copper ions form with oxygen containing groups as a result of air plasma treatment. All sorbents indicated

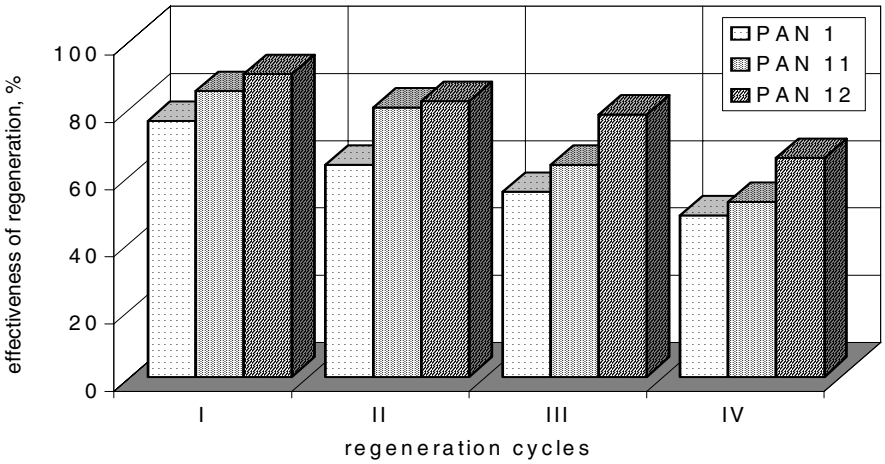

Figure 4 Effectiveness of PAN1, PAN11 and PAN12 regeneration related to Cu(II)

reduction of regeneration effect after each elution cycle. The strong binding of Cu (II) ions with nitrogen in the functional groups of ethylenediamine and ammonia modified PAN1 and PAN 11 sorbents is probably the reason for the low regeneration which was approx.50% after the IV the cycle. A comparison concerning sorption uptake related to Cu (II) ions was made between plasma and chemically modified PAN sorbents and is shown in table 4. The data for chemically modified PAN sorbents are taken from our previous experiments[24-26]. The sorption uptake of plasma modified sorbents with best sorption characteristics related to copper ions is comparable with some of PAN1 - 1,20mgeq/g is competitive to the uptake of AMCAPAN 1 sorbent, which indicated best sorption characteristics among all previously investigated chemically modified sorbents.

Table 4 Sorption uptake of modified AN copolymer sorbents related to Cu (II) ions

Sorbents	Concentration of AN copolymer%	Coagulation bath	Modification agent	Cu (II) sorption uptake, mgeq/g	Refer.
AMCAPAN	18	distilled water	15%NaOH+ 15% NH_2OH	0.90	24
AMPAN	18	distilled water	10% NH_2OH	0.77	24
CAPAN	18	distilled water	20%NaOH	0.51	24
AMCAPAN 1	9	20% DMF	15%NaOH+ 15% NH_2OH	1.20	25,26
PAN 1	9	20% DMF	Ethylenediamine plasma	1.20	in this study
PAN 11	9	20% DMF	Ammonia plasma	0.98	in this study
PAN 12	9	20% DMF	Air plasma	1.00	in this study

Conclusion

In this study plasma modified AN copolymer beads have been obtained and sorption characteristics have been investigated towards Cu (II) ions from aqueous solutions. High sorption uptake was exhibited for PAN1 (1,20mgeq/g), PAN 11(0,98mgeq/g) and PAN 12 (1,00 mgeq/g) modified with ethylenediamine, ammonia and air plasma under 5 Pa vacuum. These sorbents possess good sorption characteristics and are comparable with chemically modified ones. They can be used successfully for sorption of copper ions from aqueous solutions.

References

1. Onsoyen E, Skaugrud O (1990) J Chem Tech Biotechnol 49: 395
2. Chu K (2002) J Hazardous Materials 90(1):77
3. Wu F,Tseng R, Juang R (2000) J Hazardous Material 73: 63
4. Dalang F, Buffle J, Haerdle W (1984) Environmental Sci and Technol. 18 (3): 134
5. Simeonova A (2004) Scientific conference with international participation "Stara Zagora'2004" 1: 354
6. Atanasova M, Jordanov V (2000) J the University of Chem.Technol and Metallurgy 35:73

7. Veli S, Pekey B (2004) Fresenius Environmental Bulletin 13:244
8. Lin S, Lai S, Leu H (2000) J Hazardous Materials 76:139
9. Kull K , Steen M, Fisher E (2005) J Membr Sci 246: 203
10. Tang J, He N, Jan M, He Q, Chen H (2004) Colloids and Surfaces A 242: 53
11. Gray J, Norton P, Griffiths K (2003) Appl Surface Sci 217: 210
12. Vigo F, Nicchia M, Uliana C (1998) J Membrane Sci 36 :187
13. Ozdemir Y, Hasirci H, Serbetci K, (2002) J Material Sci 13: 1147
14. Liu Ch, Cui N, Brown N, Meenan B (2004) Surface and Coatings Technology 187: 311
15. Yang S, Gupta M (2004) Surface and Coatings Technology 187: 172
16. Kaminska A, Kaczmarek H, Kowalonek J (2002) Eur Polym J 38: 1915
17. Mc Kenzie D, Mc Gee K, Ruch P, Bilek M, Gan B (2004) Surface and Coatin Technology 186(1-2):239
18. Ilarionov I, Silchenkov D,Kostina T, Dovbii E, Zverev M (1995) Zn Prikl Khim 68: 312
19. Barash A (1995) Khim Volokna 3:289
20. Silchenkov D, Ilarionov I, Zverev M (1995) Khim Volokna 2: 589
21. Kalyanova N, Barash A, Zverev M (1995) Khim Volokna 4:6
22. Kalyanova N, Barash A, Zverev M (1997) Khim Volokna 1:13
23. Stefanova R (1997) Third black sea international conference of environmental protection technologies Varna Bulgaria: 574
24. Godgevargova Ts, Simeonova A, Dimov A (2001) J Appl Polym Sci 79: 283
25. Godgevargova Ts, Simeonova A, Dimov A (2002) JAppl Polym Sci 83:3036
26. Simeonova A, Godjevargova Ts, Dimov A (2001) Intern Sci -Pract.Conference" Industry-Technology- Environment" Moscow Russia: 675
27. Vladkova D (2001) Some possibilities for polymer surface modification Univ of Chem Technology and Metalurgy Sofia Bulgaria