

Synthesis of a Novolac-Based 3-Aminopropylsiloxane Resin and Its Application for the Removal of Cu^{2+} , Cr^{3+} , and Ni^{2+} from Electroplating Wastewater

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ABSTRACT: Novolac resin was modified with 3-aminopropyltrimethoxysilane to obtain phenol-formaldehyde-aminopropylsiloxane resin (PF-APS). Fourier transformation infra-red spectra, thermogravimetric analysis, elemental analysis, and pH-metric titration were used to characterize PF-APS. Its chemical formula was suggested to be $\text{C}_{14}\text{H}_{12.49}\text{N}_{0.1}\text{O}_2\text{Si}_{0.1}$. The resin shows high experimental metal ions uptake capacity within short time of equilibration. The metal capacity was determined by atomic absorption spectrometry to be 0.787 mEq Cu/g. Maximum separation efficiencies of Cu^{2+} , Cr^{3+} , and Ni^{2+} from aqueous solutions on PF-APS were at pH 8.0 and time of stirring 60 min; 94.0%, 90.8%, 83.2%, respectively. No significant interference from the background ions Na^+ , Cl^- , and SO_4^{2-} was observed on the separation process. The heavy metal ions were eluted using 0.01 mol L^{-1} EDTA at 65°C releasing $>94\%$ of the separated metal ions. The method of separation was applied successfully to remove the heavy metal ions Cu^{2+} , Cr^{3+} , and Ni^{2+} from electroplating wastewater from Dekirmis, Dakahlia Governorate, Egypt. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40993.

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INTRODUCTION

Environmental contamination of heavy metals ions has already become a serious problem all over the world, which threatens environment and human health.^{1,2} Therefore, the removal of heavy metal ions from industrial effluents is imperative, prior to disposal in nature. There are a variety of techniques that can be used for removing heavy metal ions including adsorption,^{3,4} chemical precipitation,^{5,6} ion exchange,⁷ and membrane separation.⁸ Ion exchange technique is one of the common methods that are preferably used for treatment of aqueous wastes because of its selectivity, simplicity, using of nontoxic materials and recyclability. For this purpose, a variety of novel ion exchangers are recently reported such as chelating resins,⁹ and modified mesoporous silica^{10–13} that can selectively remove the hazardous ions. Unfortunately, major limitations are the cost of synthesis, slow extraction kinetics, hydrolysis and/or small capacity.

Novel modified matrices with amino-groups have attracted a great attention to metal uptake. Pearson's hard–soft, acid–base (HSAB) principle states that hard (Lewis) acids prefer to bind to hard (Lewis) bases, whereas soft (Lewis) acids prefer to bind to

soft (Lewis) bases.¹⁴ RNH_2 is considered to be hard Lewis base according to Pearson's HSAB principle. Selecting RNH_2 as functional groups should create a sorbent which displays affinity for sorption of hard Lewis acid, such as copper(II) ions. Lam et al.¹⁵ demonstrated that Cu(II) was selectively removed by MCM-41 containing NH_2 -sorption sites. An amine functionalized activated carbon was reported to selectively remove Cu^{2+} with an affinity order for metal ions of $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$ with a saturation loading capacity of 0.86 mmol of Cu g^{-1} .¹⁶ Abou-El-Sherbini et al.¹⁷ also reported the separation of Cu^{2+} on zirconia or titania covered 3-aminopropylsilica gel.

The phenol-formaldehyde (PF) polymers, the first synthetic ion-exchange resins according to the pioneer work of Baekeland,¹⁸ are seen as a preferred support because of their simple route of synthesis, low cost, and unlimited storing time without further cross-linking. However, a suitable toughening is needed for most practical purposes, so that PF's are also referred to as two-stage resins.¹⁹ Novolac (typically with a molar excess of phenol with formaldehyde, commonly 1.25 : 1) is a PF in which phenols are linked together by alkylidene bridges without functional groups apart from phenolic hydroxyl groups and cannot cure on their own.

Many modifications of PF resins are used as ion exchanger to remove heavy metals. PF resin functionalized with sulphonic and carboxylic acids with capacities 3.0 and 1.1 mEq g⁻¹, respectively, is used for the removal of Pb²⁺, Co²⁺, and Mn²⁺ metal ions from aqueous solutions yielding metal capacities of 0.180, 0.086, and 0.058 mEq g⁻¹ with the equilibration time ~ 3 h.²⁰ The copolymer resin o-APDF has been synthesized by condensing o-aminophenol and dithioamide with formaldehyde in 1 : 1 : 2 molar ratio in presence of 2M hydrochloric acid as catalyst. The polymer showed higher selectivity for Fe³⁺, Cu²⁺, and Ni²⁺ than for Co²⁺, Zn²⁺, Cd²⁺, and Pb²⁺ ions with equilibration time 3–5 h.²¹ Schiff bases were prepared by condensing o-phenylenediamine with o-, m-, and p-hydroxybenzaldehydes. Condensing these phenolic Schiff bases with formaldehyde affords the chelating resins in high yields. These resins are loaded with Cu²⁺, Ni²⁺, and Fe³⁺ ions with equilibration time 24 h.²² Samal et al.²³ reported the synthesis of chelating resins by condensing a phenolic Schiff base derived from 4,4'-diaminodiphenylmethane and o-hydroxyacetophenone with formaldehyde or furfuraldehyde. The resins readily absorbed transition metal ions, such as Cu²⁺ and Ni²⁺, from dilute aqueous solutions. Also, Cd²⁺ adsorption from tap water was studied using secondary amino-functionalized weakly basic anion exchangers based on PF (Duolite A7, ion exchange capacity of 2.0) and the polyacrylic-divinylbenzene resins (Purolite A830 and A832). PF anion exchangers were reported to exhibit a marked superiority over the other types of anion exchangers.²⁴ Despite the good separation efficiencies of PF-based ion exchangers for heavy metal ions, these methods are occasionally expensive and/or complicated, and the resin may have low sorption capacity, swelling ability or long equilibration time.

Among the toughening materials, organosiloxane polymers are preferred for their excellent thermal and thermo-oxidative stabilities, moisture resistance and low stress, partial ionic nature, low surface energy, and low toxicity.^{25–28} In the present study, we report a cheap, and easy process for the synthesis of a selective ion-sorbent using aminopropylsilane as a hardener and functionalizing agent for a Novolac resin. Its sorption behavior towards Cu²⁺, Cr³⁺, and Ni²⁺ ions is studied and applied for the treatment of electroplating industry effluents.

EXPERIMENTAL

Materials

All chemicals are of analytical grade otherwise stated. Phenol (Aldrich, 99+ %), formaldehyde aqueous solution (commercial, 37%), oxalic acid, and sodium hydroxide (98%) were used. 3-Aminopropyltrimethoxysilane (APTMS, ≥98.0%) was purchased from Diamond Advanced Material of Chemical. Different concentrations of Cu²⁺, Cr³⁺, and Ni²⁺ solutions were prepared from a stock of 100 mg L⁻¹ solution prepared from analytical grade chloride salts. Sodium chloride and sulfates are from Shanghai Chemical Reagent, Shanghai, China. No further pH adjustment of these solutions is made.

Equipments

IR spectra were recorded on a Perkin-Elmer 883 infrared spectrophotometer (Norwalk, CT), using KBr pellet. A Perkin Elmer model 3110 atomic absorption spectrometer (AAS) equipped

with Varian multielement hollow cathode lamps and an air-acetylene burner was used for the determination of metals. An automatic VARIO EL ELEMENTAR instrument was used to determine the percentage of C, H, and N. The pH of each sample solution was adjusted by NaOH and HCl solutions, by using an Orion pH/mV meter combined Ross glass pH electrode. Thermogravimetric analysis (TGA) was performed on a SDT Q600 (TA Instruments, USA) thermal analyzer at a heating rate of 10°C min⁻¹ in air. The pH-metric titration measurement was performed using a Metrohm automatic potentiometer 848 Titrino. 95 mg of PF-APS was added to 5 mL of 0.0192 g Eq L⁻¹ HCl, 0.5 g Eq L⁻¹ KCl + 25 mL H₂O with titration rate of 0.5 mL min⁻¹ and titrated against 0.013 g Eq L⁻¹ KOH at 25°C.

Methodology

Synthesis of PF-APS. Novolac-PF is synthesized according to the procedure illustrated in the literature.²⁹ Two moles of phenol (188 g), 138 g of 37% (wt/wt) formaldehyde (1.7 mol), 3.7 g of oxalic acid are thoroughly dissolved at room temperature then heated at 100°C for 3 h with stirring under reflux. Then, 0.094 g of sodium hydroxide is added and, subsequently, the reaction mixture is dehydrated under a reduced pressure for 60 min. Thereafter, the temperature is stepwise raised from 100°C to 150°C and 17.93 g of APTMS is added within an hour and the mixture is stirred until the temperature is reduced to 120°C. The by-product alcohol is removed under a reduced pressure for 30 min then the reaction mixture is stepwise heated to 150°C. An amber opaque resin (Yield 201 g, 92.7% of the theoretical) and about 7 g of alcohol was obtained.

Uptake Capacity. The ion exchanger capacity of PF-APS was determined by adding 100 mg of PF-APS to 100 mL of 100 mg L⁻¹ of Cu²⁺, as chloride, solution followed by stirring for 24 h and the pH was controlled to be 5.5 by NaOH and HCl solutions. The suspension was then filtered and the capacity was determined from the loss of metal concentration in the filtrate.

Batch-Mode Separation Process of Cu²⁺, Cr³⁺, and Ni²⁺ on PF-APS. The given data are the average of three replicates. The effect of pH was studied by suspending 100 mg of PF-APS with constant stirring for 10 min in 40 mL of 100 mg L⁻¹ of Cu²⁺, Cr³⁺, or Ni²⁺ as chlorides at the desired pH values. The suspensions were filtered and the filtrates were acidified with ~0.2 mL of concentrated HNO₃ to prevent precipitation of residual metal ions as hydroxides. Then the concentration of the investigated metal ions was determined by AAS. The distribution coefficient (K_d) is determined using the equation:

$$K_d = \frac{C_{i,ex} (\mu\text{g g}^{-1})}{C_{sol} (\mu\text{g mL}^{-1})} \text{ mL g}^{-1} \quad (1)$$

where $C_{i,ex}$ is the metal concentration in the ion exchanger (solid phase) and C_{sol} is the metal ion concentration in the solution phase.

Effect of stirring time was studied at the optimum pH value; 8.0 ± 0.1 using the same conditions applied previously then the optimum pH (8.0 ± 0.1) and time of stirring (60 min) were applied in all the following studies.

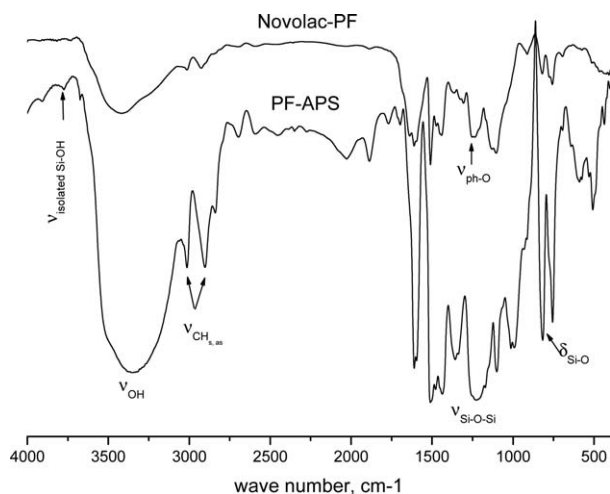


Figure 1. IR absorption spectra of Novolac-PF and PF-APS.

The possible interfering effects of wastewater background were investigated by stirring 0.2 g of PF-APS resin in 100 mL of 25 $\mu\text{g mL}^{-1}$ of Cu^{2+} , Cr^{3+} , and Ni^{2+} , simultaneously, in presence of 0.01 mol L^{-1} of sodium sulfate and 0.03 mol L^{-1} of sodium chloride at optimum pH and stirring time. The solutions were filtered, and then the filtrates were analyzed by AAS for determining Cu^{2+} , Cr^{3+} , and Ni^{2+} .

The recovery of the loaded metal ions on PF-APS was studied by stirring 0.2 g of PF-APS in 100 mL of 25 $\mu\text{g mL}^{-1}$ of Cu^{2+} , Cr^{3+} , and Ni^{2+} at optimum pH and time of stirring. The loaded resin was washed with distilled water then the metal ions were eluted with 25 mL of 0.1, 0.5 or 1 mol L^{-1} HCl. Then, the eluates were analyzed by AAS. Also, 0.001, 0.002, and 0.01 mol L^{-1} EDTA were investigated as eluent with and without 0.1 mol L^{-1} HCl at room temperature and at 65°C.

Application to Wastewater Samples. Samples of 5 L from wastewater effluents were obtained from electroplating work-

shops in Dakahlia. The samples were filtered using a sintered glass G4, and then were analyzed with AAS. A total of 100 mg of PF-APS was added to 100 mL of the sample; the pH value was adjusted to 8 ± 0.1 and stirred for 60 min then filtered. To the filtrate another 100 mg of the ion exchanger was added, the pH value was again controlled, the sample was stirred for another 60 min and filtered. The filtrate from the second process was analyzed by AAS for Cu^{2+} , Cr^{3+} , and Ni^{2+} .

RESULTS AND DISCUSSION

Characterization of PF-APS

IR Spectra. The FTIR spectrum of the Novolac-PF is given in Figure 1. The C-H stretching vibration bands are observed at 2923 and 3000 cm^{-1} . The strong band around 1250 cm^{-1} is characteristic of $\nu_{\text{ph-O}}$. The bands at 912 cm^{-1} (asymmetric ring stretching in which C-C stretches during contraction of C-O bond), 819 and 752 cm^{-1} (OOP bending of ring C-H bonds of aromatic ring) are typical of the Novolac group.³¹ The bands at 3100–3650, 1644, 1610, 1511, and 1106 cm^{-1} are assignable to stretching of OH, bending of molecular H_2O , C-C stretching in C_6 ring (doublet) and the ph-O vibrations, respectively. The IR absorption spectrum of PF-APS shows new bands at 3772, 1594, 1358, 1165, 990, 931, 819, 592, and 500 cm^{-1} which are assignable to isolated ν_{OH} (SiOH), free NH_2 scissoring, $\nu_{\text{C-N}}$, ν_{as} (Si-O-Si), $\nu_{\text{Si-O}}$ (Si-O-C), ν_{SiOH} , $\delta_{\text{Si-O}}$,^{30–32} asymmetric stretching of Si-C and $\delta_{\text{Si-O-Si}}$, respectively. The bands attributed to $\nu_{\text{ph-O}}$ and ph-O vibrations, are red-shifted in PF-APS to 1223 and 1097 cm^{-1} , respectively, probably because of replacement of ph-O-Si with ph-OH.³⁰ The absorption bands observed in the range 2830–3000 cm^{-1} are assignable to different C-H symmetric (ν_s) and asymmetric stretching (ν_{as}) vibrations.³⁰

Elemental Analysis. The results of the elemental analysis of PF-APS indicated that the found analysis of C, 73.72; H, 5.54; N, 0.67% are slightly lower than the calculated results; C, 77.5; H, 5.81; and N, 0.68% with respect to the used molar ratios of phenol/formaldehyde/APS; 2 : 1.7 : 0.1, respectively. This may

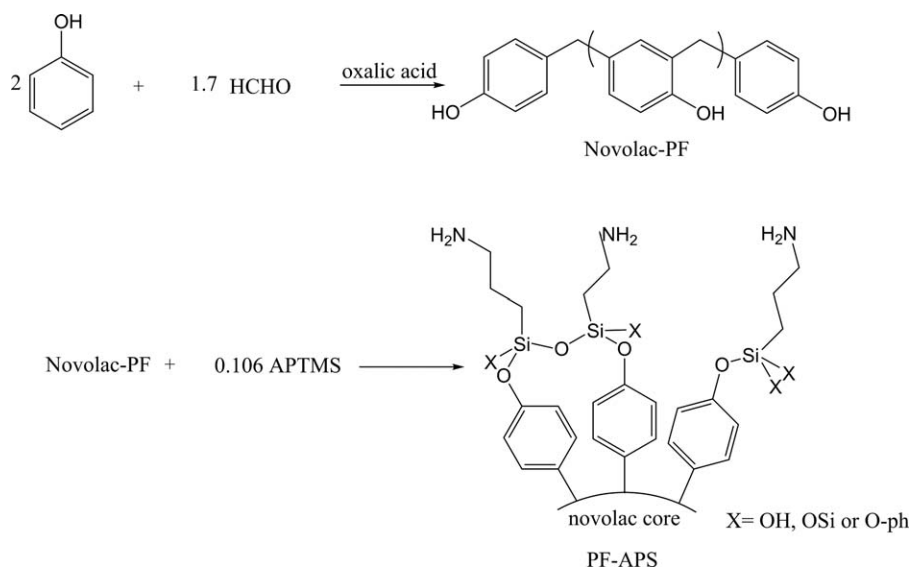


Figure 2. Scheme of formation of PF-APS.

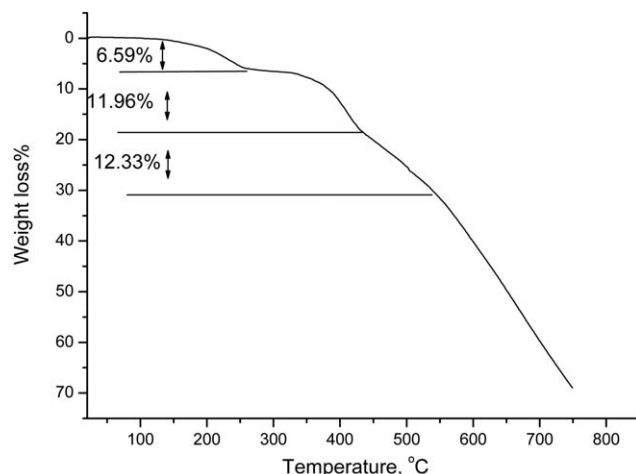


Figure 3. TGA of PF-APS.

be probably because of the presence of adsorbed water. The expected and experimental results are still comparable as the differences are less than 5%, which may be because of the presence of adsorbed water or free silanol groups. Accordingly, the formula of PF-APS is suggested to be $C_{14}H_{12.49}N_{0.1}O_{2}Si_{0.1}$ as shown in Figure 2.

Thermogravimetric Analysis. The TGA curve of PF-APS is shown in Figure 3. It shows that the ion exchanger is thermally degraded in four stages. The first stage (6.59%) is attributed to the loss of adsorbed water and the aminopropyl group which ends at 246°C. The second stage (11.96%) ends at 428°C which may be because of the degradation of methylene groups (theoretical % 10.95). The third stage (12.33%) ends at 542°C and the fourth stage (38.1%) is ended at 750°C. The last stages are thought to be because of the incomplete degradation of the aromatic content. These results are in agreement with those of the IR and elemental analysis.

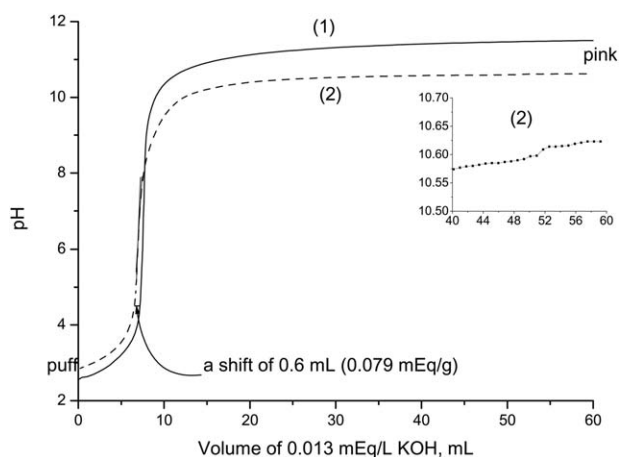


Figure 4. The pH-metric titration of PF-APS against 0.013 mEq/L KOH, (1) 30 mL 0.0032 gEq/L HCl, 0.083 gEq/L KCl (titration rate 0.5 mL/minute), and (2) 1 + 0.095 g PF-APS (titration rate 0.05 mL/min).

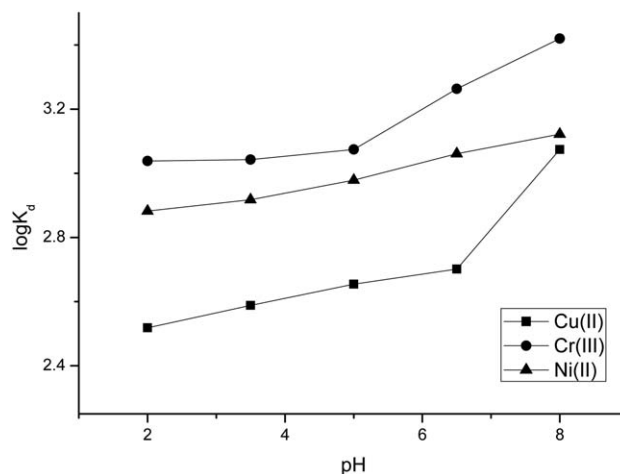


Figure 5. Effect of pH on the logarithmic values of distribution coefficients of Cu^{2+} , Cr^{3+} , and Ni^{2+} on PF-APS.

The pH-Metric Titration. Representative pH-metric titration curves of PF-APS with 0.013 mol L^{-1} KOH, in presence of 3.2×10^{-3} mol L^{-1} HCl, are shown in Figure 4. The ion exchanger shows two inflection points. The values of $pK_1^H=6.1$ and $pK_2^H=10.6$ refer to the stepwise dissociation of two protons.^{13,33} The first inflection point is because of a proton gained by the basic amino-group from HCl solution causing a 0.079 mEq/g retardation in the pH curve compared with that of 3.2×10^{-3} mol L^{-1} HCl. The protonation of the nitrogen atom was also reported for amino-functionalized solid phases as for examples the chemically modified silica-salicylaldehyde^{13,33} and for aminopropylsilica ion exchangers.¹⁷

The second inflection is suggested to be attributed to the neutralization process of the phenolic OH group. The capacity calculated at the end of this process was found to be 5.98 mEq/g of PF-APS, which is lower than that predicted from the elemental analysis (7.842 mEq/g) probably because of the slow ion diffusion within the resin network with respect to the rate of pH-metric titration and to less extent the engagement of some phenol groups in the bonding with the aminopropylsiloxane.

Capacity. The capacity measured for PF-APS using the amount of separated Cu (II) at pH 5.5 is 0.787 mmol Cu/g. This value is much lower than that found by the pH-metric method and the theoretical phenolic capacity but higher than the theoretical amino-group capacity (0.461 mmol Cu/g). This may be attributed to the presence of phenolic OH groups in tunnels and pores of the resin which cannot be accessed by the Cu^{2+} ions while it is accessible by H^+ because of the large difference in size.^{13,33} Consequently, it may be concluded that the amino-groups and some surface-located phenols are responsible for the metal sorption capacity.

The obtained capacity of PF-APS is relatively high compared with the reported PF-based ion exchangers; PF-functionalized with sulfonic and carboxylic acids has metal capacities of 0.058–0.18 mEq g^{-1} .²⁰ PF-Schiff bases showed Cu^{2+} capacity of

Table I. Effect of Stirring Time on Adsorption of 40 mL of 100 $\mu\text{g mL}^{-1}$ Cu^{2+} , Cr^{3+} , and Ni^{2+} on 100 mg PF-APS at pH 8.0

Metal ion	K_d , mL g^{-1} (adsorption, %)			
	10 min	30 min	60 min	240 min
Cu^{2+}	1163 (74.4)	2164 (84.4)	4600 (92.0)	5570 (93.3)
Cr^{3+}	2677 (87.0)	2826 (87.6)	3600 (90.0)	4795 (92.3)
Ni^{2+}	1324 (76.8)	1386 (77.6)	1981 (83.2)	2550 (86.4)

0.232–0.315 mEq g^{-1} .²² This is an important indication of obtaining a highly activated ion exchanger.

Study of the Batch-Mode Separation Condition of Cu^{2+} , Cr^{3+} , and Ni^{2+} on PF-APS

Cu^{2+} , Cr^{3+} , and Ni^{2+} are chosen to study their removal using PF-APS from waste effluents of electroplating industry as they are often used and also because of their toxicity and importance to be recovered.

Effect of pH. The distribution of metal ions between the solution and PF-APS referred to as the logarithmic values of the distribution coefficient ($\log K_d$, cm^3/g) of the metal ions Cu^{2+} , Cr^{3+} , and Ni^{2+} were determined at pH 2–8 (Figure 5). Higher pH values were avoided because Si-O-Si bonds strongly hydrolyze at $\text{pH} \geq 10$.^{17,34} The adsorption of Cu^{2+} , Cr^{3+} , and Ni^{2+} increases with the increasing of the pH value. This may be explained by deprotonating amino- and phenolic-groups, suggested from the pH-metric titration, which preferably enables these groups to bind to the metal ions rather than their precipitation as hydroxides.^{13,33} The metal ions could be successfully removed with extraction efficiency $> 74\%$ within 10 min of stirring time. Comparing these results with those obtained using PF-Schiff base resins at pH 5.7 (47–71.5% for Cu^{2+} and 0–6% for Ni^{2+}), it can be noticed that PF-APS shows higher adsorption efficiency. As the application of pH values higher than 10 is not recommended in polysiloxane applications because of possible hydrolysis,^{17,34} pH 8.0 is considered optimum for highest adsorption of Cu^{2+} , Cr^{3+} , and Ni^{2+} and is chosen for further studies.

Table II. Comparison Between Equilibration Time and Capacity of Some PF-Based Resins

Functionalizing agent	Equilibration time, h	Metal uptake capacity, mEq g^{-1}	Reference
sulphonic/carboxylic acids	3	0.058–0.180	20
o-Aminophenol/dithiooxamide	3–5	0.5–3.5	21
Schiff bases of o-phenylenediamine with o-, m-, and p-hydroxybenzaldehydes	24	0.232–0.315	22
APS	1	0.787	Present work

Effect of Stirring Time. Equilibration time is a rather important factor on practical application of waste treatment. Thus, the effect of stirring time on the adsorption efficiency of Cu^{2+} , Cr^{3+} , and Ni^{2+} onto PF-APS is studied applying the optimum pH 8.0 (Table I). Apparently, 6 hours of stirring gave a maximum adsorption of 93.3%, 92.3%, and 86.44%, respectively. However, one hour of stirring is considered optimal when comparing the close values of adsorption efficiencies 92.0%, 90.0%, and 83.2%, respectively, and the large difference of stirring times. To realize the advantages of PF-APS as adsorbent, a comparison is presented in Table II between the time of equilibration and the adsorption efficiencies with those reported elsewhere for PF-functionalized resins. Apparently, PF-APS has short time of equilibration and higher capacities. This may be attributed to that the main functionalizing agent, APS, is hydrophilic which is easily accessible by the metal ions. This short time of adsorption equilibration is known for surface-modified APS materials.^{33,34}

Effect of Interference Ions. Table III shows the effect of background ions frequently found in the electroplating waste effluents on the extraction of Cu^{2+} , Cr^{3+} , and Ni^{2+} on PF-APS. Results indicate that the presence of chloride or sulfate does not affect their adsorption efficiencies except for Ni^{2+} which slightly decreases. This slight decrease in adsorption of Ni^{2+} on PF-APS may be because of the stabilization of the octahedral $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ions in the solution phase by hydrogen bonding to sulfate ions.³⁵

From the effects of pH, time of stirring, and interference ions, to obtain almost complete removal of the metal ions, it is recommended to perform two successive separation batches at pH 8.0, with time of stirring 60 min to guarantee $> 95\%$ adsorption of Cu^{2+} , Cr^{3+} , and Ni^{2+} on PF-APS.

Recovery of Adsorbed Metal Ions. The recovery of the adsorbed metal ions was studied using different eluents at different temperatures to enable beneficiation of the recovered metal ions and to examine the re-usage ability of PF-APS (Table IV). High concentration of HCl was observed to decrease the

Table III. Effect of 0.01 mol L^{-1} of Sodium Sulfate and 0.03 mol L^{-1} of Sodium Chloride on the Adsorption Efficiency of 100 mL of 25 $\mu\text{g mL}^{-1}$ Cu^{2+} , Cr^{3+} , and Ni^{2+} on 100 mg PF-APS at pH 8.0 and Stirring Time 60 min

Metal ion	Adsorption (%)
Cu^{2+}	94
Cr^{3+}	90.8
Ni^{2+}	78.4

Table IV. Effect of Different Concentrations of EDTA and HCl on the Recovery, %, in Respect to the Initial Concentration and to the Loaded Amount (Between Brackets) of Cu^{2+} , Cr^{3+} , and Ni^{2+} (100 mL of $25 \mu\text{g mL}^{-1}$) Loaded on 0.2 g PF-APS at pH 8.0 and Stirring Time 60 min

Eluent			%		
			Cu^{2+}	Cr^{3+}	Ni^{2+}
HCl	0.1 mol L ⁻¹		36.2 (40.1)	7.6 (8.66)	6.0 (7.51)
	0.5 mol L ⁻¹		33.3 (36.9)	7.0 (7.97)	5.3 (6.64)
	1.0 mol L ⁻¹		27.8 (30.8)	5.0 (5.69)	3.6 (4.51)
0.1 mol L ⁻¹ HCl	+ EDTA	0.001 Mol L ⁻¹	81.3 (90.1)	8.6 (9.79)	7.2 (9.02)
		0.002 Mol L ⁻¹	83.0 (92.0)	76.0 (86.6)	9.8 (12.3)
		0.001 Mol L ⁻¹ at 65°C	84.0 (93.1)	53.2 (60.6)	39.3 (49.2)
EDTA	0.01 mol L ⁻¹		85.4 (94.7)	83.9 (95.6)	41.2 (51.6)
	0.01 mol L ⁻¹ at 65°C		88.1 (97.7)	84.0 (95.7)	75.3 (94.3)

released metal ions which may be attributed to the adsorption of the anionic chloro-complexes of the metal ions on the protonated amino-groups.^{13,33} Addition of EDTA and elevation of the eluent temperature to 65°C increased the liberation of the loaded metal ions. Almost complete elution of the loaded metal ions was achieved with 0.01 mol L⁻¹ EDTA at 65°C. It is noteworthy to mention that the Cu^{2+} -capacity of PF-APS did not remarkably change (0.724 mEq Cu/g) after repeating 20 cycles of metal ions separation and elution processes using 0.01 mol L⁻¹ EDTA as eluent. This indicates the stability of the resin and its ability for regeneration.

Application to Wastewater Effluents of an Electroplating Workshop

The treatment of wastewater effluents is the main target of this study. They are discharged from electroplating workshops which are small size enterprises located in Dakahlyia Governorate, Egypt. The workshops discharge their wastewater into the sewage network without preliminary treatment performing an ecological threat. The wastewater (25.5 m³/day) is discharged from the workshops during two working shifts. The production processes include metal forming and shaping, surface preparation (dry cleaning/acid cleaning), rinsing and surface finishing by Ni-Cr electroplating. Accordingly, the presence of herein-reported simple technology is important for the treatment of the wastewater effluents.

The optimum conditions of the extraction of Cu^{2+} , Cr^{3+} , and Ni^{2+} (pH 8.0, stirring time 60 min at room temperature) on

PF-APS were applied on 100 mL of two wastewater effluents as shown in Table V. The remained metal ions were less than the detection limit (0.005, 0.04, and 0.05 $\mu\text{g mL}^{-1}$, respectively). Accordingly, the heavy metal ions could be almost completely removed using PF-APS.

CONCLUSION

A simple and cheap method of synthesis of PF-based-aminopropylsilane ion exchange resin is reported for the removal of Cu^{2+} , Cr^{3+} , and Ni^{2+} from effluents of electroplating workshops. PF-APS shows high metal-uptake capacity [0.787 Cu(II) mEq/g] and short time of equilibration than those reported for APS-functionalized or PF-based chelating resins. The highest separation efficiencies of the investigated metal ions on PF-APS were obtained at pH value 8.0 and time of stirring 60 min; 92.0%, 90.0%, and 83.2% of the initial concentration of Cu^{2+} , Cr^{3+} , and Ni^{2+} , respectively. No significant interference is observed from ions frequently present the effluent of electroplating workshops; SO_4^{2-} or Cl^- . The recovery of the adsorbed metal ions is > 94% using 0.01 mol L⁻¹ EDTA as an eluent at 65°C as EDTA for each single batch process. Moreover, no significant capacity fading is observed after 20 cycles of separation and recovery.

The method is successfully used for the removal of the studied metal ions from the effluents of an electroplating workshop by applying two successive batch-separations.

Table V. Concentration of Cu^{2+} , Cr^{3+} , and Ni^{2+} ($\mu\text{g mL}^{-1}$) in 100 mL of Waste Effluents of an Electroplating Workshop Before and After Extraction with 2×100 mg PF-APS at pH 8.0 and Stirring Time 60 min

Metal ion	Sample (1) ($\mu\text{g mL}^{-1}$)		Sample (2) ($\mu\text{g mL}^{-1}$)		Permitted amount, ($\mu\text{g mL}^{-1}$)
	before treatment	after treatment	before treatment	after treatment	
Cu(II)	6.5	BDL	12.2	BDL	1.5
Cr(III)	8.7	BDL	8	BDL	0.5
Ni(II)	11.2	BDL	8.2	BDL	1.0

BDL means below detection limit of AAS.

REFERENCES

- Hill, M. K. *Understanding Environmental Pollution: A Primer*, 2nd ed.; Cambridge University Press: Cambridge, **2004**, 107, 199.
- Peirce, J. J.; Vesilind, P. A.; Weiner, R. *Environmental Pollution and Control*, 4th ed.; Butterworth-Heinemann: Boston, **1998**, 31, 248.
- Tahir, S. S.; Naseem, R. *Sep. Purif. Technol.* **2007**, 53/3, 312.
- Wan Ngah, W. S.; Teong, L. C.; Hanafiah, M. A. K. M. *Carbohydr. Polym.* **2011**, 83, 1446.
- Lewis, A. E. *Hydrometallurgy* **2010**, 104, 222.
- Pang, F. M.; Teng, S. P.; Teng, T. T.; Omar, A. K. M. *Water Qual. Res. J. Can.* **2009**, 44, 174.
- Da_browski, A.; Hubicki, Z.; Podko_scielny, P.; Robens, E. *Chemosphere* **2004**, 56, 91.
- de Agreda, D.; Garcia-Diaz, I.; López, F. A.; Alguacil, F. *J. Rev. Metalur.* **2011**, 47, 146.
- Chen, C. Y.; Lin, M. S.; Hsu, K. R. *J. Hazard. Mater.* **2008**, 152, 986.
- Yang, H.; Xu, R.; Xue, X. M.; Li, F. T.; Li, G. T. *J. Hazard. Mater.* **2008**, 152, 690.
- Abou-El-Sherbini, Kh. S.; Hassanien, M. M. *Sep. Sci. Technol.* **2004**, 39, 1177.
- Hassanien, M. M.; Abou-El-Sherbini, Kh. S. *Talanta* **2006**, 68, 1550.
- Abou-El-Sherbini, Kh. S.; Hamed, M., A.; Kenawy, I. M. M., Issa, R. M. and Elmorsi, R. *Talanta* **2002**, 58, 289.
- Pearson, R. G. *J. Am. Chem. Soc.* **1963**, 85, 3533.
- Lam, K. F.; Yeung, K. L.; McKay, G. *Langmuir* **2006**, 22, 9632.
- Yantasee, W.; Lin, Y. H.; Fryxell, G. E.; Alford, K. L.; Busche, B. J.; Johnson, C. D. *Ind. Eng. Chem. Res.* **2004**, 43, 2759.
- Abou-El-Sherbini, Kh.; Pape, C.; Rienitz, O.; Schiel, D.; Stosch, R.; Weidler, P. G.; Höll, W. H. *J. Sol-Gel Sci. Technol.* **2010**, 53, 587.
- Baekeland, L. H. *Ind. Eng. Chem.* **1909**, 1, 149.
- Looney, M. G.; Solomon, D. H. *Aust. J. Chem.* **1995**, 48(2) 323.
- Kamel, N. H. M.; Sayyah, E. M.; Abdel-aal, A. A. *Schol. Res. Libr. Arch. Appl. Sci. Res.* **2011**, 3, 448.
- Gurnule, W., B.; Katkamwar, S. S. *Rasayan J. Chem.* **2012**, 5, 365.
- Mohanty, D.; Samal, S. E.-J. *Chem.* **2009**, 6, 1035.
- Samal, S.; Acharya, S.; Dey, R. K.; Ray, A. R. *J. Appl. Polym. Sci.* **2003**, 88, 570.
- Zhao, X.; Höll, W. H.; Yun, G. *Water Res.* **2002**, 36, 851.
- Chojnowski, J.; Cypryk, M.; Scibioek, W.; Rozga-Wijas, K. *Macromolecules.* **2003**, 36, 3890.
- Gupta, P.; Bajpai, M. *Adv. Chem. Eng. Sci.* **2011**, 1, 133.
- Durairaj, R. B.; Lawrence, M. A.; Walkup, C. M. **2003**, US6875807 B2.
- Durairaj, R. B.; Lawrence, M. A.; Walkup, C. M. **2003**, US7259221 B2.
- Hu, X.; Zeng, J.; Dai, W.; Shi, W.; Li, L.; Han, C. *Polym. Bull.* **2011**, 66,703.
- Lambert, J. B.; Shurvell, H. F.; Lighter, D. A.; Cooks, R. G. *Organic Structural Spectroscopy*; Prentise-Hall: New Jersey, **1998**.
- White, L. D.; Tripp, C. P. *J. Colloid Interface Sci.* **2000**, 232, 400.
- Turner, R. H.; Boerio, F. J. *J. Adhes.* **2002**, 78, 447.
- Abou-El-Sherbini, Kh.; Kenawy, I.M.M.; Issa, R. M. *J. Appl. Polym. Sci.* **2003**, 88, 3159.
- Iler, R. *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry*; Wiley: New York, **1979**.
- Wells, A. F. *Structural Inorganic Chemistry*; Oxford: Clarendon Press, **1984**.