Heavy metals removal from electroplating wastewater by aminopropyl-Si MCM-41

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Abstract

The potential of removing nickel and copper from industrial electroplating wastewaters by using mesoporous materials with MCM-41 type structure functionalised with different ratios of aminopropyl groups, namely Na_{50}, Na_{25} and Na_5, were evaluated. The synthesised solids sorbents obtained were characterised by X-ray diffraction, elemental chemical analysis and IR spectroscopy. In preliminary experiments, studies were carried out to determine the optimal experimental conditions for the retention of heavy ions. Effects of concentration, optimal pH, interference with humic substances and other metals were studied for Na_5, which showed the best capacity of absorption determined by the corresponding isotherm. This material has a greater selectivity against sodium, indicating that ionic strength does not affect the extraction. Results of an application of this material to remove nickel and copper in synthetic and real industrial wastewater samples from an electrochemical industry area are shown with successful results. The lowest level of nickel and copper were observed when Na_5 was used. This observation suggests that reactive aminopropyl-Si MCM-41 and similar materials may be a promising and provide for alternative environmental technologies in the future.
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1. Introduction

The increasing level of heavy metals in the environment represents a serious threat to human health, living resources and ecological systems. Although there are many sources of heavy metals, some industrial sectors are at present those which contribute the most to environmental pollution with these toxic metals. Among such industrial sectors, the metal finishing industry is an important one due to the large number of enterprises by which is integrated as well as their geographical dispersion. The main way of contamination by these industries is the emission of liquid effluents with relatively low, although harmful metal concentrations (up to some hundreds of mg l^{-1}), among these metals, Cr, Ni, Zn, Cu and Cd are usually the most abundant ones.

These contaminants must be removed from wastewaters before discharge as they are considered persistent,

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bioaccumulative and toxic substances (US EPA, 1998). Of special technical and economic importance is the selective removing of metals derived from the discharge from electrochemical activities into industrial wastewater. In comparison with other industries, the industrial electrochemistry uses less water, hence the volume of wastewater produced is smaller, and the wastewater is highly toxic in nature because of the presence of metals such as copper, nickel, zinc, cadmium and cyanides. It is well established that the presence of heavy metals in the environment, even in moderate concentration is responsible for producing a variety of illnesses related with the risk of dermal damage, respiratory problems and several kinds of cancer, as accurately reviewed in a recent papers (Barceloux, 1999a,b).

Various treatment technologies have been developed for the removal of these metals from wastewater, depending on the concentration, such as precipitation of the metal hydroxide and filtration when higher concentration are treated (Aziz et al., 2001; Kim et al., 2001). Ion exchange using zeolites (Zamow and Murphy, 1992), clays (Reddy and Chinthamreddy, 2003) or ionic resins (Abollino et al., 2000; Yalcin et al., 2001) are generally employed when the range of contamination is low. These systems due to the degree of interaction, present a small selectivity when cationic interferences are also present. Electro-winning, is another way to remove heavy metals using electrochemical tools. The metal is recovered as pure metal, in one stage, without the necessity of sludge disposal and regeneration of saturated ion exchange resin (Njau et al., 2000). Bioremedial alternatives have been employed in contaminated industrial wastewater and groundwater, namely microalgal (Chong et al., 2000) and bacteria (Vainshtein et al., 2003). Materials such as activated carbon (Kadirvelu et al., 2000) or alumina (Cervera et al., 2003) give very good results but they have the inconvenience of high cost when pure sorbents are employed. There is an increasing trend for substituting these by unconventional metal cations removal as red mud or fly ash (Apak et al., 1998) or composting (Barker and Bryson, 2002). These are future alternatives which are starting to give good results, although their selectivity is low.

The use of materials with surface functional groups, such as functionalised MCM-41, shows improved selectivity for the removal heavy metals in wastewater. For this purpose we have developed, in this work, an effective, simple and low cost alternative employing chelating agent with aminopropyl groups incorporated on inorganic materials, which may prevent the problems associated with conventional methods. The synthesis of MCM-41 structures provide solids with several physico-chemical properties, which can be optimised for the removal process i.e. high specific area and a narrow uniform distribution of pores (Beck and Vartuli, 1996).

They are synthesised with surfactants, used as template and can be functionalised later on with different organic groups such as thiol, as previously reported for the removal of mercury from contaminated effluent stream (Mercier and Pinnavaia, 1997). Hall has extended the method of template for the direct co-condensation to synthesize MCM-41 structures containing allyl, phenyl or amino groups (Hall et al., 1999), but no applications in the environmental field have been reported yet. So far experiments were carried out at a lab scale employing aminopropyl used as solid phase extraction for the quantification of bismuth, lead, and nickel in seawater (Tokman et al., 2003).

Following the same line of research, this work introduces some alternatives in their synthesis, in order to improve their structure characteristics, and propose MCM-41 functionalised with aminopropyl groups to be employed as an alternative for the removal heavy metals in wastewater from electroplating effluent with a higher concentration of nickel and copper.

2. Material and methods

2.1. Reagents and solutions

Analytical grade reagents were employed. Cetyltrimethylammonium chloride (CTMA), tetraethylorthosilicate (98%) (TEOS), 3-aminopropyl-triethoxisilane (96%) (APTEOS), tetramethylammonium hydroxide, 25% water solution (TMAOH) and humic substances (HS) were used without further purification as supplied by Aldrich (Milwaukee, WI). All heavy metals solutions (Ni^{2+}, Cu^{2+} and Co^{2+}) were prepared in stock solutions up to 1000 ppm ($1\,g\,l^{-1}$) of metal from the corresponding nitrate salts. No further pH adjustment of these solutions was made as their natural acidity due to hydrolysis of metals (i.e. to form MOH^+ and H^+) prevented the precipitation of the corresponding metal hydroxides. High purity water was used from a Milli-Q system (Millipore, Bedford, MA) and employed throughout.

2.2. Synthesis of aminopropyl-Si MCM-41

TEOS and APTEOS were mixed, in 5, 25 and 50 molar ratio respectively in ethanol:*n*-propanol (4:1) and added to a solution of CTMA (25% in water), which was previously heated at 80 °C during 30 min and the pH was adjusted to 10 with TMAOH. The mixture was then stirred for 3 d at room temperature. The white solids obtained were centrifuged and washed with water and were referred as N_5, N_{25} and N_{50}. Cationic exchange, using a saturated dissolution of NaCl in ethanol:water (80:20), was employed to remove the CTMA used as template. This procedure was carried out three times at room temperature and the solids were recovered

by centrifugation after being washed with ethanol and air-dried at 60 °C. The solids obtained were referred to as Na₅, Na₂₅ and Na₅₀ hereafter in the text.

2.3. Procedure for nickel and copper extraction in pure and wastewater

Sorption studies were carried out by shaking a given dose, 1 g of sorbent in 100 ml of water with the respectively metal solution for a period of 1 d at room temperature in stoppered flasks, in order to guarantee equilibrium conditions. The solids were then centrifuged and metals retained in the solid were measured by atomic absorption spectroscopy. For that purpose, the materials were dissolved with 0.2 ml of hydrofluoric acid at room temperature and diluted to the measuring range of concentration. The procedure carried out for the electroplating samples was the same. All assays were carried out in triplicate and only mean values are presented.

2.4. Equipment

Powder X-ray diffraction (XRD) was recorded using Siemens D501 diffractometer using Cu K$_\alpha$ radiation and a graphite monochromator. IR spectra were recorded at room temperature by a Perkin-Elmer 883 infrared spectrophotometer (Norwalk, CT), using KBr pellet method. A Perkin Elmer model 3110 atomic absorption spectrometer equipped with Varian multi-element hollow cathode lamps and an air-acetylene burner was used for the determination of metals. The wavelengths (nm) selected for the determination of metals were: Cu, 324.8 nm; Ni, 232.0 nm; Co, 240.7 nm, respectively.

3. Results and discussion

3.1. Characterisation of aminopropyl-Si MCM-41 materials

In order to check the effect of the surfactant extraction procedure, the compounds were analysed by elemental chemical analysis showing the best results in the solids with the higher density of aminopropyl groups (where C/N molar ratio is near three for N₅ and higher in the another ones). However, a significant reduction of the percentage of carbon is observed due to the removal of surfactant, but a residual fraction remain in all cases, which is responsible for the upper C/N molar ratio obtained. Given that for the N₅₀ and N₂₅ the amount of aminopropyl groups is minor, the increase of the C/N molar ratio value due to the presence of this residual surfactant is more important. After the removal of the surfactant used as template, the cylindrical pores, typical of MCM-41 solid, are free and the aminopropyl groups which functionalises the inorganic wall, are accessible

Table 1
Characteristic of the different materials synthesised

Material	% C	% N	C/N	d_{100} (Å)	S_{BET} (m² g⁻¹)
N₅₀	16.76	1.65	10.15	40.4	–
N₂₅	16.20	1.88	8.61	43.6	–
N₅	16.64	1.65	10.08	45.0	–
Na₅₀	6.72	0.76	8.84	43.0	869
Na₂₅	6.54	0.94	6.95	48.0	881
Na₅	6.32	1.84	3.43	48.0	649

to the retention of chemical species, which can interact with transition metal ions by complexation process.

A parameter that denotes the accessibility of these pores is the BET specific area of these materials determined from N₂ adsortion–desorption isotherm at 77 K (Brunauer et al., 1938). In all the cases, type IV reversible isotherms are obtained, which are characteristic of mesoporous materials MCM-41 type. High specific area values are obtained from Na₅₀, Na₂₅ and Na₅ (Table 1). While similar values were obtained for Na₅₀ and Na₂₅, for Na₅ the observed value is lower. This can be explained by a distortion in the structure of this more dense material induced by the presence of the aminopropyl groups. This is consistent with XRD patterns, N₅₀,
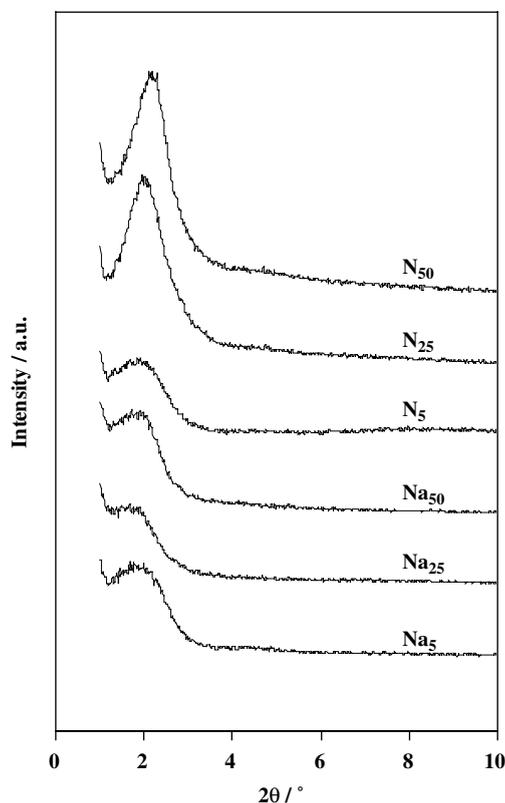

Fig. 1. XRD pattern of different materials.

N_{25} and N_5 show an intense signal at low angle, corresponding at d_{100} diffraction (Fig. 1). When the aminopropyl density increases, this signal shows shift to low angles or decrease in intensity due to the presence of a minor ordered structure caused by aminopropyl groups that have a negative impact on the template effect of the surfactant. The interaction between aminopropyl groups and the surfactant cylindrical micelles produce an increase in the size by expansion of cylindrical galleries of surfactant formed into inorganic material. After CTMA extraction (Na_{50}, Na_{25} and Na_5 materials), diffraction peaks remain although their intensity decreases, showing a decreasing in the structure order. The results we obtained are similar and consistent with those obtained by using a calcinations process for removing the surfactant (Hitz and Prins, 1997). All these results are summarised in Table 1.

3.2. Absorption isotherm of nickel and copper in Na_5, Na_{25} and Na_{50}

The behaviour of Na_5, Na_{25} and Na_{50} in the retention of nickel and copper uptake at 25 °C were investigated, showing a typical profile of a Langmuir isotherm in the absorption process. In the case of Cu^{2+}, as showed in Fig. 2a, their absorption increases when the ratio TEOS:APTEOS decreases, because of an increase of
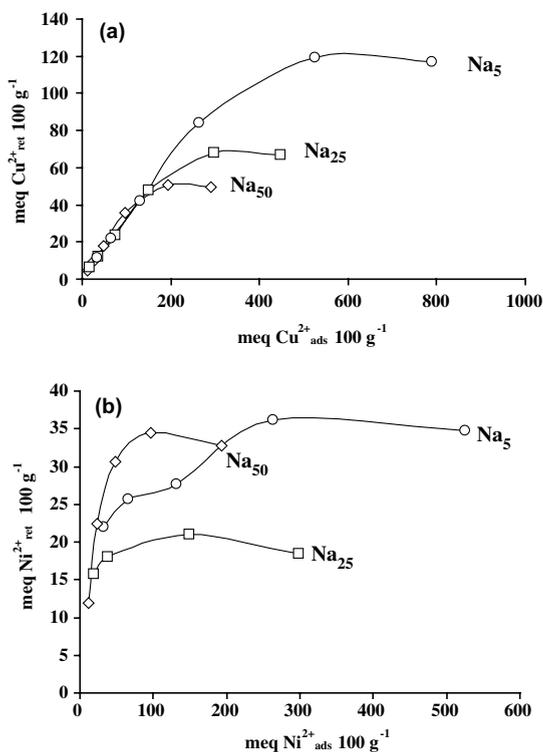
aminopropyl groups present on the structure, reaching the saturation of copper at 128, 75 and 54 meq 100 g^{-1} of sorbent respectively. For Ni^{2+}, under the same experimental conditions, the retention isotherms are showed in Fig. 2b, reaching the saturation at 36, 21 and 34 meq 100 g^{-1} of sorbent. In both cases, Na_5 shows the best retention of metal. Comparison with the data in the literature, clays show a similar behaviour when are used as cationic exchange with values around 100–150 meq 100 g^{-1}, such as vermiculite (Domenech, 1995) or 70–95 meq 100 g^{-1} for montmomorillonite (Mercier and Detellier, 1995), but their selectivity for these cations are limited. A good review of the application of different natural sorbents have been published recently (Babel and Kurniawan, 2003).

According to this behaviour, an increasing concentration of amino groups increases the retention process, in fact for the Ni^{2+} and Cu^{2+} retention, Na_5 presents a higher efficiency, which can be explained mainly by the presence of aminopropyl groups that are able to react with metals. However this relation does not hold in the case of Ni^{2+} retention by Na_{25}. Although Na_{25} contains two times more aminopropyl groups than Na_{50}, its Ni^{2+} removing efficiency is substantially reduced with respect to that of Na_{50}.

Fig. 3 represents the efficiency of the retention of Ni^{2+} for each material. According to the molar ratio of Ni^{2+} retained/aminopropyl groups presents on the sorbent (Ni^{2+}/N retained), we can observe that for Na_{50}, it is three times higher than in the another solids, showing in this synthesised solid. The interaction between nickel and aminopropyl groups is 3:5 while in the another materials it is 1:5, which indicates that not all the amino groups interact with Ni^{2+} cations, given that in this case, the ratio obtained will be 1:1. On the other hand, in the case of Na_{50}, the presence of aminopropyl groups is minor, the separation is significant, interacting with only one nickel while in the another,
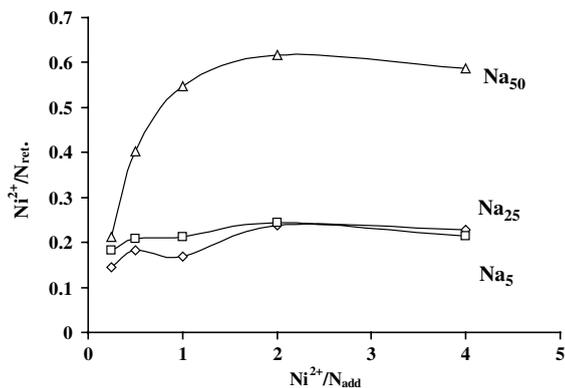

Fig. 2. Absorption isotherm onto Na_{50}, Na_{25} and Na_5 for (a) Cu^{2+} and (b) Ni^{2+} at pH = 4.

Fig. 3. Efficiency in the retention of Ni^{2+} for Na_{50}, Na_{25} and Na_5 materials in function of the ratio Ni^{2+}/aminopropyl at pH = 4.

Na$_5$ and Na$_{25}$, this distance is less, and the three amino-propyl groups interact with each nickel cation, showing a similar performance. However, for Cu^{2+}, the retention in all the sorbents for the Cu^{2+} retained/aminopropyl groups presents molar ratio close to 1, which explains the major retention of Cu^{2+} when compared with Ni^{2+}, as shown in Fig. 2a and b. In this case, the evolution of the retention with the amount of aminopropyl groups present is as predicted, given that an increase of ligands groups involves an increase of metal retention.

This relation data show that the dependence of Ni^{2+} and Cu^{2+} retention by aminopropyl groups is due to a complexation mechanism, evidencing their ligand properties, as will be show in detail, studying several factors which can influence its retention as pH, concentration and presence of interferences.

3.3. Influence of pH and concentration

The dependence of sorbent Na$_5$ (which present a major capacity for the retention of Cu^{2+} and Ni^{2+}) with the pH and concentration of metal, was evaluated. As for the influence of pH, and concentration, the M^{2+}/N molar ratio added was 1, to avoid the excess of metal, corresponding to a value of 131 meq 100 g^{-1} of sorbent. Given that the mechanism of retention can be the complexation of cations with aminopropyl groups present in the sorbent, the pH is a parameter to optimise, because if it is low, the amino groups will be protonated and thus unusable as ligand. Fig. 4 shows the dependence of pH with the amount of metal retained. In this graph, we can observe that at a range of pH under 3, the decrease of the retention of metal is drastic, thus the working pH range recommended is 3–4. At higher pH, the precipitation of metal hydroxides can occur on the basic surface of material, blocking the pores and decreasing the retention, mainly in the case of Cu^{2+} ions. Fig. 5 shows the concentration effect in the Ni$^{2+}_{ret}$/N by Na$_5$, it is observed
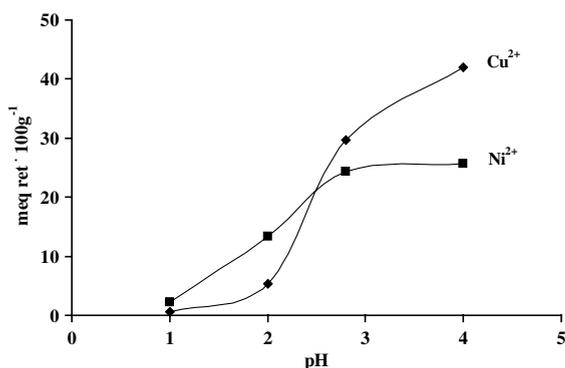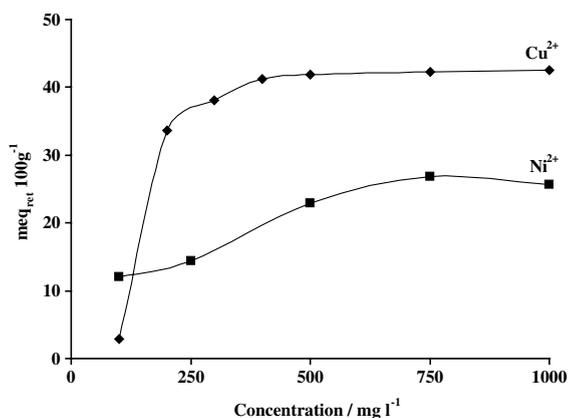
Fig. 5. Effect of the nickel concentration.

that on decreasing the amount of absorbent material, the removal of the metal decreased as well, and very fast at a concentration below at 750 and 400 mg l^{-1} for Ni^{2+} and Cu^{2+} respectively, while at upper revels it is constant. This difference between these two concentration range, for which the retention is maximal, is influenced by the upper value of the respective formation constant by each complex, as mentioned in the next section, where the effect of the interferences presence on retention is discussed.

3.4. Interference study

To estimate and investigate the selectivity in the extraction of Ni^{2+} by Na$_5$, interference study is an interesting parameter to be verified. The main mechanism of absorption in this kind of material is by means of complexation. For that purpose, the influence in the extraction procedure has been studied and optimised for Ni^{2+}. If there are any other analytes in the matrix with a higher formation constant (K_f) than the nickel complex, they will be retained preferentially in the same way.

The nickel retention was analysed in the presence of other cations (M^{n+}) such copper, cobalt or sodium. The results obtained for the nickel extraction with different molar ratio of Ni^{2+}/M is presented in Fig. 6. Clearly, it is seen that the sodium cations do not affect the nickel extraction, therefore it can be deduced that this process is independent of the ionic strength, and the complexation is the only responsible for the retention. Thus metals belonging to alkaline and alkaline-earth groups that do not form complex with aminopropyl groups do not interfere. On the other hand, when copper or cobalt is present in the solution, a decrease in the efficiency of this procedure is drastically denoted for the first metal. This can be explained based on their respective K_f, according to the Irving–Williams series (Shriver et al., 1992), which establishes the bond strength between a given ligand
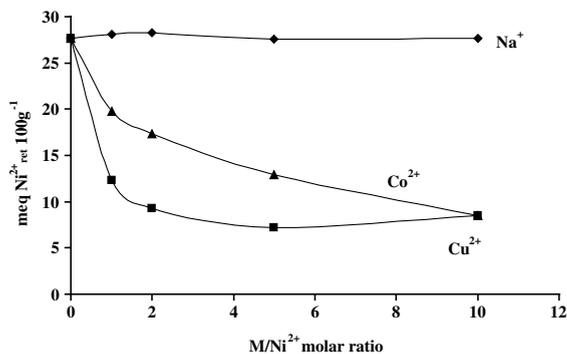
Fig. 4. Influence of pH in the efficiency extraction of nickel by Na$_5$.

Fig. 6. Influence of interferences in the efficiency of nickel extraction by Na_5.

Fig. 7. Application of Na_5 in wastewater from electroplating industry.

(despite the nature of the ligand) and a series of metal cations, which is in the sequence $Co^{2+} < Ni^{2+} < Cu^{2+}$ and consequently, K_f $(Cu^{2+}) > K_f$ $(Ni^{2+}) > K_f$ (Co^{2+}). Thus, the copper complex is more stable, and a high negative slope is observed in solution unless the complex between aminopropyl and cobalt is less, obtaining a moderate and good efficiency in presence of this one.

Given that this work is focused on the application of this material in the retention of inorganic cations contaminants, the influence of interferences on the metal retention is completed with the influence of HS, which is present in natural water coming from the degradation of natural organic mater. For both metals, HS was loaded to a solution with a molar ratio M^{2+}/aminopropyl = 1, equivalent to 131 meq 100 g^{-1} of sorbent, in the range of concentration to 10 mg l^{-1}. As a result, the retention of Ni^{2+} or Cu^{2+} did not decrease significantly and the retention was maintained in the range of 48 meq 100 g^{-1} of sorbent for Cu^{2+} and 27 meq 100 g^{-1} for Ni^{2+}, which indicates that these cations are preferably complexed by the sorbent face than the HS.
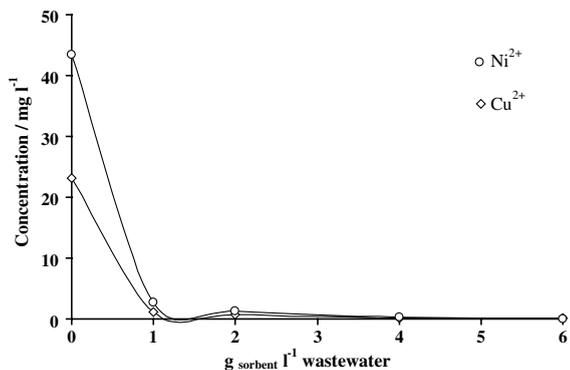
3.5. Application to wastewater

In accordance with the results obtained previously the procedure was applied to wastewater, employing Na_5 as the removing material. Sampling was done in the vicinity of an electrochemical industry (Sorinsa, SA) sited in Montilla, Córdoba (Andalucía, Spain). Electroplating processes are present in a great diversity of product as car components, jewellery, electronic devices or furniture. From the original piece to the finished article, several steps are involved in the electroplating process. One of them, the wash after the electrolytic bath, and the efficiency of this step have repercussion in the quality of the final product and the electrolytic bath composition. For the control of this composition, the purity of the water used in the cleaning processes is necessary, and high volumes of water are used. This water must be therefore treated by a depuration system before it is recovered or removed, although the concentration of corresponding metallic ion is relatively low.
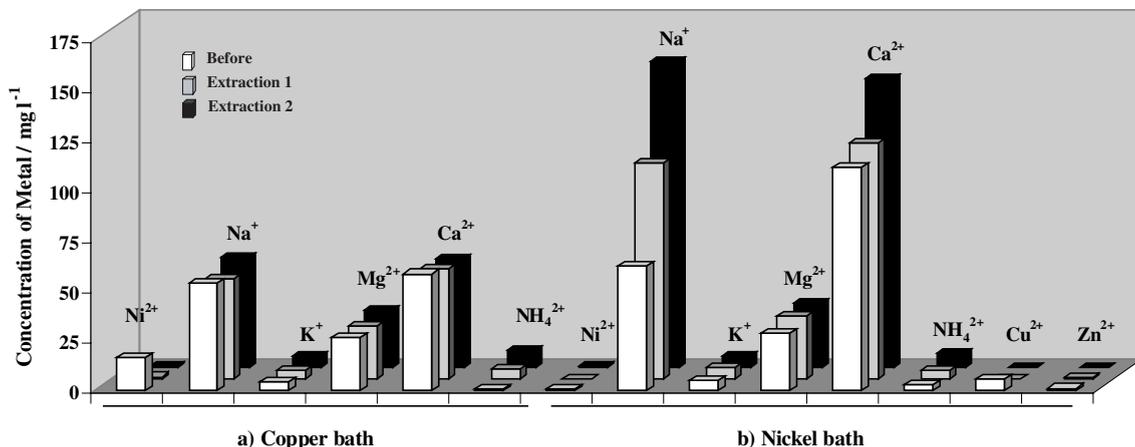

Fig. 8. Application of Na_5 in a real electroplating baths. (a) Electroplating bath of Ni^{2+} and (b) electroplating bath of Cu^{2+}.

On the other hand, the nickel and copper baths are the most used, as final coating, as well as intermediate steps of other metallic finishes as gold or brass.

As previously exposed, the Na_5 material can act as sorbent of these cations, thus it was tested for the removal of Ni^{2+} and Cu^{2+} from wastewater coming from the washing bath. Fig. 7 shows the effect of the Na_5 material in two pattern different electroplating baths from the activities performed in the industry mentioned above. From these results we can deduce that for a sorbent/wastewater of $1 \, g \, l^{-1}$, the concentration of metal in both cases is below the limit imposed by law. The effect of the use of this sorbent in the other components of the wastewater was also studied and the effect is shown in Fig. 8, the selectivity and the reproducibility of this sorbent for the retention of Cu^{2+} and Ni^{2+} in the presence of other ions, in the case of a real wastewater samples.

4. Conclusions

Synthesised mesoporous materials, Na_5, Na_{25} and Na_{50}, were explored in absorption experiment to investigate their capacity to remove heavy metals such as Ni^{2+} and Cu^{2+} in wastewater from industrial effluents. The possible use of aminopropyl-Si MCM-41 as effective sorbents in the removal of heavy metals from contaminated water was investigated. The results indicate that the aminopropyl-Si MCM-41 presents a good potential as an alternative material for heavy metal removal from aqueous solutions versus metals which do not react such as alkaline and alkaline-earth. Due to the high toxicity of these cations, the materials reported in this paper applied to their removal from wastewaters could be envisaged.

Acknowledgement

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