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Binding metal cations and nitrate anions by new synthetic support: Castor Oil-AAc-AAm

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Summary

A new synthetic gel was obtained by bulk polymerization of castor oil, acrylic acid and acrylamide. This paper describes the ability of this gel to uptake heavy metals and nitrate ions from aqueous solutions as demonstrated in our laboratory. Determinations, before and after batch experiments, were carried out using atomic absorption and UV spectroscopy. These results showed that $A1^{+3}$, Fe^{+3} and Pb^{+2} ions were effectively adsorbed.

Introduction

During the last few decades, the expansion in industrial activity, has enhanced environmental decay. Consequently, environmental pollution has become one of the major hazards threatening our daily lives. In particular, the occurrence of heavy metal ions in sewage water may be detrimental to human and all living organism. Many methods have thus been proposed for the removal of heavy metal ions, such as chemical precipitation, activated carbon adsorption, membrane filtration and ion exchange [1]. On the other hand, the application of fertilizers has brought about high contaminant in many water ways because of the higher amounts and their contamination are not admissible to the industry. The general, the limiting tolerance for nitrates and nitrites is lower than 50 mg/l and 0.1 mg/l, respectively [2-4].

However, massive removal of heavy metal ions due to the high process cost is often undesired. The need for effective and economic removal of toxic/valuable [5] heavy metal ions from sewage and industrial and mining wastewaters resulted in a search for unconventional methods and materials that might be useful to revert this process. Many natural products such as clays and wood bark or farming by-products available at little or no cost are capable of binding heavy metal ions by adsorption, chelation, or ion exchange. The use of agricultural by-products such as tree bark, peanut shells, and walnut expeller meal by Randall et al., Kumar et al., wool by Friedman et al., cotton by Roberts et al. and ricestraw, paddy husks, sugarcane bagasse, and wheat chaff by Kumar et al. for the sorption of toxic heavy metal ions has been reported [6-9].

Accordingly and following our research line [10-11] we have looked into the synthesis of polymeric materials containing monomeric residues and/or attachment ligands with special functional groups able to act as chelating agents [12-13], absorbents or ion-exchange groups. A new hyperbranched polymeric support, was synthesized from inexpensive monomers such as castor oil, acrylic acid (AAc) and acrylamide (AAm). After obtaining the new polymeric resin, a hyperbranched product, we focused on behavior as flocculating agent with retention of metallic ions in water.

Hyperbranched polymers are macromolecules that have received considerable attention. These polymers are developed by one-step polymerization resulting in less regular structures. An undesiderable feature of the one-step polymerization is the loss of control in molecular weight distributions and possible intramolecular cyclizations. A branched acrylate derivated from castor oil was obtained by emulsion polymerization of latexes and proposed for commercial application in architectural coatings [3], [14].

Experimental

Materials

The following chemicals were purchased and used: castor oil, (Cicarelli), acrylic acid p.a., AAc, (BASF, Argentina), acrylamide, AAm, for synthesis (Merck), benzoyl peroxide (Riedel of Häen) and the solvents utilized for washing of the new product were pro-analyses. The metal salts were provided by Sigma. Buffers used: pH = 4.0 (50 mL of 0.1 molar potassium hydrogen phthalate + 0.1 mL of 0.1 molar HCl) and pH = 7.0 (50 mL of 0.1 molar potassium dihydrogen phosphate + 29 mL of 0.1 molar Na(OH)).

Instruments

Elemental analyses were carried out by Atlantic Mycrolab Inc. IR spectra were recorded on a Nicolet 5-SXC spectrometer. Thermogravimetric analysis was carried out using a Perkin-Elmer 1B with heating rate of 10°C/min under Ar atmosphere and with Al_2O_3 as reference. Atomic absorption determinations were made on a Polarized Zeeman Absorption Hitachi spectrophotometer. Scanning electron microscopy was performed on a Philips SEM 501B instrument. TGA, Atomic Absorption and Scanning Electron Microscopy were carried out at the Centro de Investigaciones de Materiales y Metrología (CIMM) (Córdoba, Argentina).

Methods

Quantitative determination of the free acid groups were made using a titration method and a setback with 0.1N NaOH using phenolphthalein as indicator. Determinations of nitrate ions were carried out using a Shimadzu UV-260 spectrophotometer measuring at 400 nm.

The swelling indices and percentages were measured following a modified technique of the ASTM Norm D 3616-77.

Percentage of Swelling

$$(DS\%) = [(Wsw - Wdr)/Wdr] * 100 \qquad (\mathbf{1})$$

Swelling index

$$(SwI) = Wsw/ Wdr \qquad (\mathbf{2})$$

Where Wsw and Wdr are the weights of the swollen and dried sample respectively.

Volume Swelling Ratio

$$(qv) = Vsw/Vdr \qquad (\mathbf{3})$$

Where Vsw and Vdr are the volume of the swollen and dried sample respectively.

Synthesis of the Castor Oil-AAc-AAm.

Bulk polymerization was carried out using a ratio of eq. 2:2:1 of Castor Oil, AAc and AAm, respectively in a closed stirred steel reactor for 18 hours using benzoyl peroxide (5%w/w) as initiator. The temperature was increased 10°C/h, starting from 40°C up to 100°C.

The solid yellowish product obtained was washed with benzene, ethanol and distilled water. Finally, a white-yellowish solid product was collected, milled and sifted using sieves of 70-100 mesh. After dry, it was studied by elemental analysis, Thermogravimetric analysis and IR spectroscopy. Swelling in different solvents and pH were measured and the amount of acid groups present was determined.

Retention experiments of the metal and nitrate ions.

Batch metal uptake experiments were performed using metal chloride and metal nitrate solutions. In order to carry out this method, approx. 50 mg of Castor Oil-AAc-AAm was swelled (0.01 g/mL) in water at neutral pH (acid form) and the same weight of the product was swelled in NaOH solution (carboxylate form). Then, 25 mL of different salt solutions were added observing an immediate flocculation. The total of reaction was mixed for 4 h more at room temperature in order to complete adsorption. Higher times of contact not indicate changes in adsorption.

The supernatant was separated by decantation and the solid was washed with 30 mL of water. The total supernatant was diluted with distilled water to a known volume. The chelated metal ion amount was determined by measuring the difference of the quantity of metal ion added and the non chelated metal ion (Tables II and III). By the same method, the amount of nitrate ion adsorbed was determined (Table IV).

Results and discussion

Nowadays, a very important problem is the supply of drinking water. Many efforts have been made to find more effective and economical methods, although anything of importance has yet been commercialized. Consequently, this circumstance has prompted researchers to search for new synthetic polymeric supports with carboxyl, hydroxyl or other groups that might serve this purpose [11].

In order to prepare an inexpensive copolymer with reactive groups able to retain metal and nitrate ions, castor oil was copolymerized with acrylic acid and acrylamide looking for a new hyperbranched polymer *Castor Oil-AAc-AAm.*

Characterization of Castor Oil-AAc-AAm.

The elemental analysis showed the presence of 54.54 % C, 6.35 % H, 8.14 % N and 30.97 % O. Determination of the carboxyl groups of the polymeric matrix yielded values of 3.50 meq. per 1 g of dry solid product.

The IR spectrum of Castor Oil-AAc-AAm showed the following signals: 3500 - 3700 cm^{-1} (stretching of O-H of the acid or N-H of the acrylamide), 1448 cm^{-1} (combined band from C-O of the hydroxyl group of the acid and N-H group of the amide) and 1208 cm^{-1} (stretching C-O of the ester).

The presence of acrylic acid, acrylamide and castor oil is evidenced by the occurrence of a strong and wide band between 1730 and 1500 cm^{-1} attributable to the carbonyl groups of the monomers. The deconvolution of the signal showed three bands at 1729, 1640, 1537 cm^{-1}.

The swelling indices were carried out in water at pH 4 and pH 7 (buffers, see Materials, in Experimental), dichloromethane and acetonitrile. Results are shown in Table I

The swelling indices could not be carried out in alkaline solutions because dissolution of the gel was noticed.

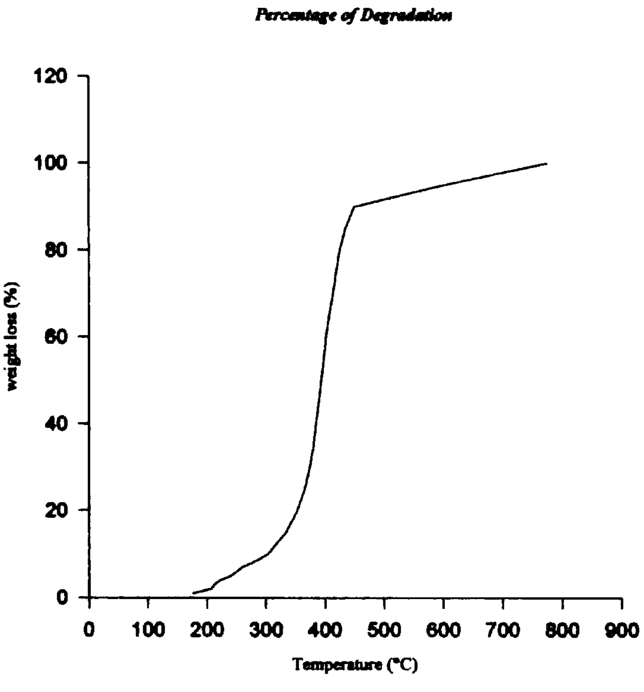

Figure 1. Curve of percentage degradation of Castor Oil-AAc-AAm

Weight loss-temperature curve resulting from raising temperature on *Castor Oil-AAc-AAm* at a constant rate in argon atmosphere, is plotted in Figure 1. Losses become detectable at 176°C (1% of total weight) and 50% of the weight loss occurs at 394°C.

Table I. Swelling indices and percentage values from Castor Oil-AAc-AAm

Solvent	DS (%)	SwI	Qv
Acetonitrile	64.94	1.65	1
Dichloromethane	4.60	1.05	1
Buffer pH 4	147.87	2.48	1
Buffer pH 7	139.23	2.39	1

DS: swelling degree, SwI: swelling indices, qv: volume swelling ratio

Heavy metal and nitrate ions retention capabilities.

The results of retention capabilities of metal ions using *Castor Oil-AAc-AAm* are listed in *Table II.* As observed, the gel in these experiments has excellent chelating properties removing heavy metal ions from aqueous solutions. Flocculation phenomenon was observed after addition of the metal solution to the carboxylate of the hyperbranched polymer according to the results of the following assays.

Table II. Retention of metal ions from aqueous solutions in batch experiments using *Castor Oil-AAc-AAm*

Salts	Acid form		Carboxylate form	
	Initial Amount (mmol metal ion)	Sorbed Amount (mmol metal ion/g gel)	Initial Amount (mmol metal ion)	Sorbed Amount (mmol metal ion/g gel)
$Mg(NO_3)_2$	0.95	0.56	0.50	0.062
$Zn(NO_3)_2$	0.49	0.28	0.17	NS
$Pb(NO_3)_2$	1.69	1.04	0.94	NS
$Fe(NO_3)_3$	2.50	1.59	1.08	0.37
$Al(NO_3)_3$	14.47	7.69	6.45	3.38
$FeCl_3$	2.26	1.87	1.07	0.39
$AlCl_3$	1.14	0.70	6.35	3.69

NS: non specified. In this case flocculation phenomena was not observed.

Adsorption uptake assays from the acid form and carboxylate form of the gel, showed similar range of efficiency in the removal of heavy metal ions provided by nitrate or chloride anions: $Al^{+3}>>Fe^{+3}>Pb^{+2}>Mg^{+2}>Zn^{+2}$. The Al^{+3} ion proved to be the most retained by *Castor Oil-AAc-AAm*. When comparing metal nitrate and metal chloride ($Fe(NO_3)_3$-$FeCl_3$ and $Al(NO_3)_3$-$AlCl_3$), the difference in adsorption pointed out that this retention was influenced by the hydration state of the anion present.

Nitrate anions in different complexes, tend to intervene by different ways increasing the stability of the complex, allowing donor ligands (H_2O, NH_3, etc.) to form additional coordination bonds with metals [15].

Due to a higher crosslinking of trivalent cations, their adsorption was more important compared to the values of divalent cations (Mg^{+2}, Zn^{+2} and Pb^{+2}). To examine the competition between various heavy metal ions for the substrate binding sites, approx. 100 mg of the *Castor Oil-AAc-AAm* was swelled in water and solubilized in NaOH solution. Then they were added with aqueous solution containing either $ZnCl_2$, $AlCl_3$ and $FeCl_3$, in equimolar ratio (0.01 meq / mL).

The results of selective adsorption of metals from a mixed solution of Fe^{+3} / Al^{+3} / Zn^{+2} are listed in *Table III*. These experiments have shown the same range uptake of the ions in both gels, acid and carboxylate form.

Table III. Competitive adsorption of Zn^{+2} / Al^{+3}/ Fe^{+3} from a mixed aqueous solutions in batch experiments.

Salts	Sorbed Amount (mmol metal ion/g gel)	
	Acid Form	Carboxylate Form
$ZnCl_2$	0.24	0.32
$AlCl_3$	1.09	1.44
$FeCl_3$	0.52	0.60

The results of the selective isolation of metals from mixed solution of Zn^{+2}, Al^{+3} and Fe^{+3} showed a clear preference for Al^{+3} ion (approx. 80% initial conc.). Moreover, the order of adsorption was Al^{+3}>>Fe^{+3}>Zn^{+2}. Results corresponding to the capability of *Castor Oil-AAc-AAm* gel to adsorb nitrate ion are shown in *Table IV*.

These assays have shown an important capability for resin adsorption. Approximately 99%-100% of the initial concentration was removed from water solutions. In this case the NO_3^- from aluminum nitrate showed the highest level of uptake for the gel (in its acid and carboxylate form). From these results we observed a nitrate-metal correlation in agreement with retention order still observed from corresponding metal ions assays.

Table IV. Nitrate ion chelated from aqueous solutions in batch experiments

Salts	Acid Form		Carboxylate Form	
	Initial Amount (mmol NO_3^-)	Sorbed Amount (mmol NO_3^-/g gel)	Initial Amount (mmol NO_3^-)	Sorbed Amount (mmol NO_3^-/g gel)
$Mg(NO_3)_2$	0.47	0.45	0.50	0.45
$Zn(NO_3)_2$	0.24	0.23	0.17	0.13
$Pb(NO_3)_2$	0.86	0.84	0.93	0.91
$Fe(NO_3)_3$	1.90	1.80	1.60	1.58
$Al(NO_3)_3$	11.00	10.97	9.50	9.49

Scanning Electron Microscopy

The micrograph of the surface of the resin before adsorbing Fe^{+3} and Al^{+3} from nitrate and chloride salts is shown in Figure 2, with the micrograph of the surface after adsorption being shown in Figures 3-6. The initial roughness of the surface was smoothed by the adsorption of metal and nitrate ions.

Conclusions

A hyperbranched ubiquitous and inexpensive polymer was obtained from castor oil, acrylic acid and acrylamide, which seems to be an excellent substrate for the binding and almost quantitative removal of a number of heavy metal and nitrate ions from water. Retention assays were carried out in batch experiments, a very simply method.

Results obtained showed that Al^{+3}, Fe^{+3} and Pb+2 ions were truly adsorbed about the same order from the acid or the carboxylate form of the hyperbranched polymer. However, divalent ions (Mg^{+2} and Zn^{+2}) were only slightly adsorbed by the resin.

Although the order of the adsorption affinities for various ions is not unique to any particular adsorbent, in general it increases with atomic valence and number. When the atomic valence was the same as can be seen from the order of Fe^{+3} and Al^{+3} ions, the adsorption was higher while the atomic number was lower. Scanning electron microscopy in Fig. 3 and Fig. 4, showed porous with sufficient space to interchange cations and anions. Fig. 5 and Fig. 6 showed changes in the surface respect to Fig. 2. There are evidences of ionic interactions in these complexes during the formation of flocs, with the intervention of metals; different anions solvated by water molecules must be taken in account. The differences amounts in adsorption of cations and the capacity to remove the total of nitrate ions was demonstrated. Different adsorption of other cations and anions are object of further work in order to see, if changes in sizes of anions or cations, charges or other characteristics, justify differences in adsorption.

Figure 2. The surface of the Castor Oil -AAc-AAm before adsorption metallic salts (x 5000)

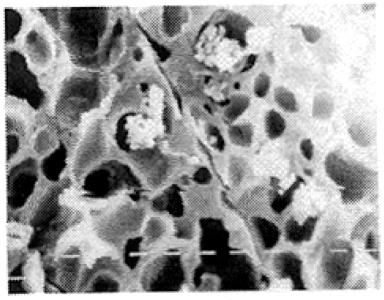

Figure 3. The surface of the Castor Oil-AAc-AAm after adsorption $Fe(NO_3)_3$ (x 5000)

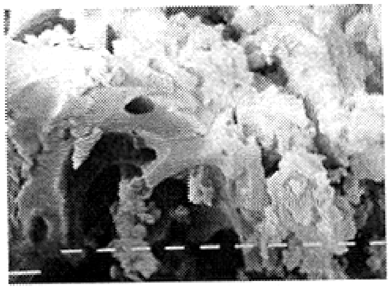

Figure 4. The surface of the Castor Oil-AAc-AAm after adsorption $FeCl_3$ (x 5000)

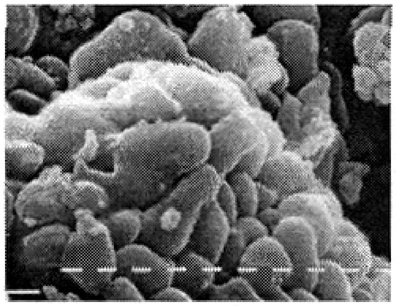

Figure 5. The surface of the Castor Oil-AAc-AAm after adsorption Al $(NO_3)_3$ (x 5000)

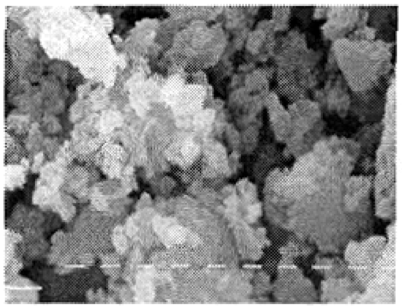

Figure 6. The surface of the Castor Oil-AAc-AAm after adsorption Al Cl_3 (x 5000)

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