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Removal of heavy metals from aqueous media using native cassava starch hydrogel

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Graft copolymers of cassava starch and acrylonitrile were synthesized in aqueous solution using ceric ammonium ion as the initiator. Saponification of grafted copolymer was done by reaction with sodium hydroxide and precipitated with methanol. Grafting was confirmed by Fourier transform infrared spectroscopy (FTIR). The grafted copolymer and the hydrolyzed graft copolymer (hydrogel) were used as sorbent for the uptake of heavy metals from the aqueous media. The sorption capacity was evaluated by measuring the extent of sorption of nickel, copper, and leads metals ions, under equilibrium conditions. Using the sorption isotherm models, the Freundlich model was found suitable because of good fitness and equilibrium data yielded the following ultimate capacity values for the sorbent of the grafted copolymer: 54 mgPb/g, 64.5 mgCu/g and 71.1 mgNi/g and for the hydrogel: 72 mgPb/g, 76.6 mgCu/g and 86.5 mgNi/g. Hydrolysis increases the sorption affinity of grafted copolymer toward metal ions. Acid stripping with 2% HCl resulted in 99.6% metal recovery for the hydrogel and 52.2% for the grafted copolymer. This shows the ability of the product to be reused, upon drying between treatments.

Key words: Acrylonitrile, cassava starch, grafted copolymer, heavy metals, hydrogel, sorption.

INTRODUCTION

The removal of heavy metal ions from various water resources is of great scientific and practical interest. A wide range of physical and chemical processes are available for the uptake of heavy metals and organics from aqueous media, such as electro-chemical precipitation, ultrafiltration, ion exchange and reverse osmosis (Rengaraj et al., 2001; Yurlova et al., 2002; Benito and Ruiz, 2002). A draw back with precipitation is sludge production. Ion exchange is considered a better alternative technique for such a purpose. However, it is not economically appealing because of high operational cost. Sorption using commercial activated carbon (CAC) from petroleum based materials can remove heavy metals and organics from aqueous media, such as Cd (Ramos et al., 1997), Ni (Shim et al., 2001), Cr (Ouki et al., 1997), Cu (Monser et al., 2002). However, CAC

remains an expensive material for heavy metal uptake and organics, which has caused interest to be shifted to the use of other low cost and readily available agricultural products as precursor for the preparation of value added products.

Synthetic cross linked polyacrylates, hydrogels have been used to remove heavy metals toxicity from aqueous media. However, application of these synthetics on large scale may not be a practical solution due to exorbitant costs. A hydrogel is defined as a cross-linked hydrophilic polymer or copolymer that is capable of imbibing a considerable quantity of water, up to swelling equilibrium. Hydrogels have widespread application in bio-engineering, biomedicine, pharmaceutical, veterinary, food industry, agriculture, photographic technology, and other fields (Saraydın et al., 1995; Maziad, 2004). The first step in the preparation of hydrogels is the selection of a highly hydrophilic or even water-soluble polymer (Essawy and Ibrahim, 2004). In recent years, the syntheses of hydrogels with chelating groups have received considerable attention for rapid and inexpensive

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metal ion separation and concentration. It was determined that crosslinked polymeric materials having functional groups such as carboxylic acid, amine, hydroxyl, amidoxime, and sulfonic acid groups could be used as complexing agents for the removal of metal ions from aqueous solutions (Karadag et al., 1995). The main advantages of such materials are easy loading and, in most cases, stripping of cations with simple chemicals and reusability.

Since polysaccharides are abundant from renewable sources and are relatively inexpensive, safe (non-toxic) and amenable to both chemical and biochemical modifications. It is not surprising that they find widespread and extensive use. Graft copolymerization is a unique method among the techniques for modifying natural polymers mostly polysaccharides. Polysaccharides graft copolymers have been prepared in order to add new properties to the natural polymer with a minimum loss of native properties (Fanta and Doane, 1986).

In view of the growing interest and research activity in the use of renewable agriculturally derived products as extenders and replacement for synthetic petroleum-based polymers, incorporation of other monomers/polymers into polysaccharides will not only reduce our dependence on petrochemical derivatives, but also provides improved materials which will biodegrade rapidly in the environment.

Relatively few or no data are available in the literature on the removal of heavy metals from aqueous media using native cassava starch hydrogel in developing countries. The present communication is an attempt to evaluate the equilibrium sorption properties of grafted and hydrolyzed grafted copolymers, using Nigerian grown native cassava starch. The combination of the useful properties of acrylonitrile and that of Nigerian grown native cassava starch, could introduce a modified biosorbent matrix with many application and superior sorption capabilities.

MATERIALS AND METHODS

Acrylonitrile (AN) used was supplied by B.D.H. as reagent grade and was distilled under reduced pressure and stored in the dark at 5°C before use, cassava starch was sourced from a local cassava starch processing factory in Benin City, Nigeria; Analar grade Cerium ammonium nitrate (CAN) was supplied by BDH, Poole, England.

Synthesis of graft copolymers

Dried starch (5 g) in a 50 cm³ volume of distilled water was gelatinized by heating at 85°C for 30 min in a 500ml conical flask in a thermostatic water-bath. The homogenous, soft, opaque paste obtained or gelatinized starch was cooled to 33°C. In a typical reaction, solution of ceric ammonium nitrate (CAN) freshly prepared by dissolving 20 mmol/l, molar concentration of CAN salt in 3 ml of 1.0 M nitric acid was added and 3.65 mol of acrylonitrile (AN) monomer was added to the flask and the mixture was stirred. The

polymerization reaction was allowed to proceed at 40°C for 3 h under stirring. The polymerization procedure was based on the method described by Pourjavadi et al. (2007)

The whole volume of the resulting mixture was divided into two equal portions. One portion was reserved for saponification to obtain the hydrogel and the other portion was precipitated with 200 ml of 95% ethanol. The precipitate was separated by filtration and dried in an oven at 30°C for 24 h, (Hashem et al., 2005).

Hydrolysis of the grafted copolymer

The half portion of the grafted copolymer produced was hydrolyzed by adding 9 ml, 0.7 M NaOH in a weighing bottle and mixed well. The bottle (loosely stoppered to permit escape of ammonia) was then placed in an electric oven at 75°C. The slurry was stirred for 2 h, with the color changing from white to maroon to pale yellow. The slurry was allowed to cool and was neutralized to pH 6.5 with 2% hydrochloric acid. The slurry was filtered on Whatman No. 54 filter paper on a Buchner funnel, and the product was washed with water (500 ml). The product was dewatered with acetone (500 ml) and then washed with ether (100 ml) and dried for 2 h under vacuum.

Characterization of the cassava starch-g-P(AN) hydrogel

The dried product was extracted with dimethylformamide for 30 h to remove the free polymer (FP)/homopolymer (polyacrylonitrile). The grafted starch was dried for 4 days to obtain a constant weight. The percent graft yield (%G) and percent graft efficiency (%GE) were calculated using the Equations (1) and (2), (Lanthong et al., 2006).

$$\% G = \frac{\text{final starch wt} - \text{initial starch wt}(5g)}{\text{initial starch wt}(5g)} \times 100 \quad (1)$$

$$\% GE = \frac{\text{final starch wt} - \text{initial starch wt}(5g)}{\text{Total polymer wt after reaction} - \text{initial starch wt}(5g)} \times 100 \quad (2)$$

Results are as presented in Table 2

Infrared analysis

IR spectrophotometer was used as a tool to follow up changes in graft reaction. Spectral of cassava starch and copolymers after grafting, and after saponification recorded on a Nicolet impact 410 FTIR spectrophotometer using a KBr pellet and the spectral sheets are presented in Figure 1.

Swelling measurement

Swelling of the hydrogels were measured by the free swelling method, (Weaver et al., 1977) and expressed as a water retention value (WRV) calculated in grams of water per grams of dry polymer. In a typical measurement, 0.1 g was immersed in 100 ml of distilled water for 30 min and allowed to stand. The swollen hydrogel was then separated from unabsorbed water by screening through a weighed No. 41 filter paper in a funnel by normal gravity force. Corrections were made for the water retention of the filter paper, that is, by repeating the measurement using blank filter paper in contact with water. The hydrogel was allowed to drain on the paper for 10 min and the paper was then weighed to determine the weight of water which caused swelling of the hydrogel. Swelling Equation characteristics was calculated as g/g using the following 3:

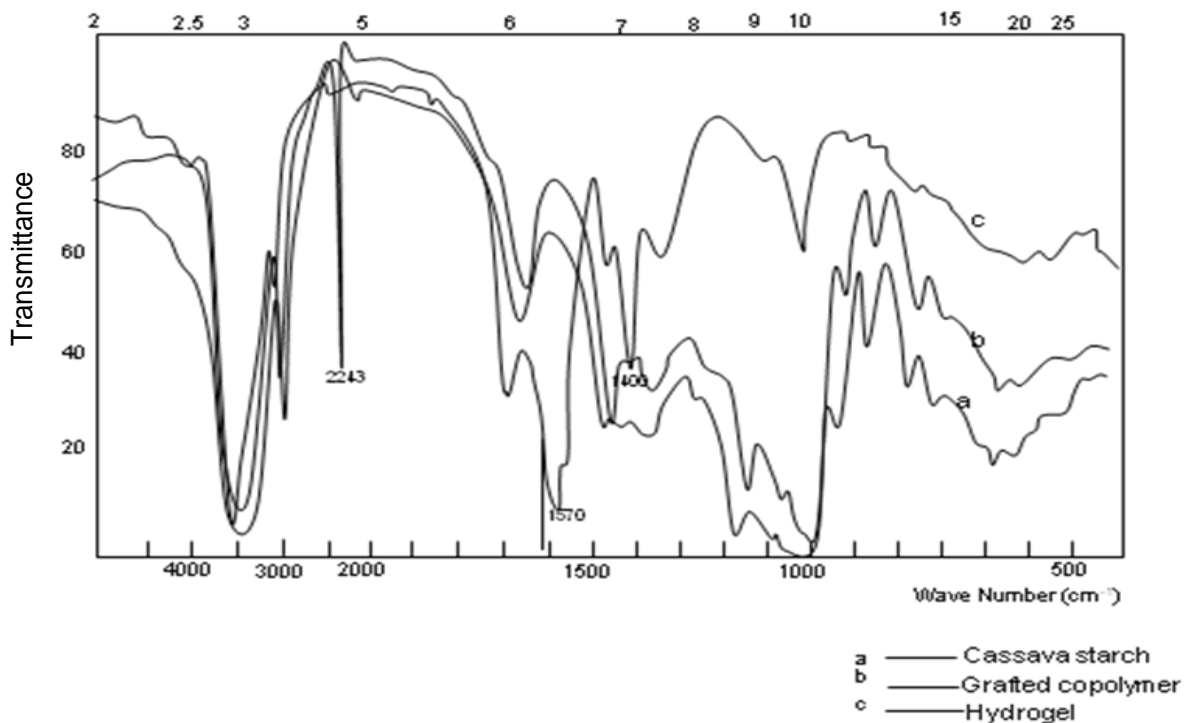


Figure 1. FTIR spectral of (a) cassava starch, (b) grafted copolymer and (c) hydrogel.

$$\text{Water retention value (g/g)} = \frac{(W_2 - W_1)}{W_1} \quad (3)$$

Where, W_2 and W_1 are the weights of water swollen hydrogel and dry absorbent in grams, respectively. Results are as presented in Table 2.

Equilibrium uptake of Heavy metal ions from aqueous media

Batch equilibrium experiment was carried out using the grafted copolymer and hydrogel as the sorbents. Sorption of metal ions concentrations were determined by using the perkin Elmer bulk scientific (Analyst 200) Atomic Absorption Spectrophotometer (AAS). Sorption was carried out by stirring 0.5 g of the sorbent materials respectively for 30 mins in 100 ml aqueous media containing varying concentrations of ions of (Lead, Copper, and Nickel) respectively.

Lead Nitrate ($\text{PbNO}_3)_2$, Copper Sulphate (CuSO_4), Nickel Nitrate hexahydrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ [BDH, England] were used as the source of Lead (II), Copper (II), and Nickel (II) for the aqueous media. The Pb, Cu, and Ni stock solutions were prepared by dissolving 80 mg of $\text{Pb}(\text{NO}_3)_2$, 124 mg of CuSO_4 , and 196 mg of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 1000 ml of deionized water respectively.

The change in Pb(II), Cu(II), and Ni(II) concentrations due to sorption was determined by AAS after filtration, that is, the sorbents were separated from unadsorbed metal ions concentration by screening through a filter paper in a funnel. The sorbent was allowed to drain for 10 mins and the concentration of the unadsorbed metal ions concentration determined using AAS. The sorbed metal ions concentration in the sorbents is evaluated as:

The metal ions sorbed = Initial metal ions concentration in solution – unadsorbed metal ions concentration determined by AAS.

The used polymer material was acid stripped with 2% HCl, to determine the desorption rate of the hydrogel and grafted copolymer. The extent of uptake and retention capacity of the grafted copolymer and hydrogel are expressed in percentage as follows (Abd-Alla et al., 2007):

$$\text{Metal ions uptake \%} = \frac{\text{amount of metal in polymer}}{\text{amount of the metal in the feed}} \times 100 \quad (4)$$

$$\text{Metal ions retention} = \frac{\text{amount of metal ions in polymer}}{\text{weight of dry polymer}} \quad (5)$$

RESULTS

Characteristics of the grafted copolymer and hydrogel

The characteristics of the grafted copolymer are shown in Table 1. The water absorption (WRV) of the grafted copolymer gave high water absorption of 382 g g^{-1} . A study of the reaction indicates that grafting is associated with the homopolymer formation and that saponification converts the same grafted poly (AN) chain and homopoly (AN) chain with cyano group ($-\text{C}\equiv\text{N}$) as the main group to both amide ($-\text{CONH}_2$) and carboxylate ($-\text{COONa}$) groups. The nitrile groups of PAN were converted to a mixture of hydrophilic carboxamide and carboxylate groups during alkaline hydrolysis, followed by *in situ* cross-linking of the grafted PAN chains. More PAN led to

Table 1. Characteristics of the grafted copolymer and the hydrogel.

Characteristics	Results
Water retention value (g/g)	382
Grafting efficiency (%)	88.55
Grafting yield (%)	92.18
Add-on percentage	55.5
Free polymer (%)	10.25
pH	8.5

more carboxamide and carboxylate groups being generated from the alkaline hydrolysis of PAN.

Spectral characterization (Infrared analysis)

The IR spectra for starch, starch-g-PAN before and after grafting and after the alkaline hydrolysis are presented in Figure 1.

Spectral characterization (infrared analysis)

The IR spectrum of cassava starch in Figure 1a, gives absorption bands an –OH broad at 3400, and single intermolecular polymeric band the C–H stretching at 2930 cm^{-1} , and C–O–C stretching in the 1,000–1100 cm^{-1} band, characteristic of amylase contained in the starch. The presence of the nitrile group at 2243 cm^{-1} and the strong asymmetrical stretching at 1570 cm^{-1} and a weak symmetrical stretching at 1430–1390 cm^{-1} coupled with characteristics bands at 3400, 1000–1100 cm^{-1} for amylase contained in the starch indicated the occurrence of grafting in Figure 1b. However, the appearance of the nitrile group at 2243 cm^{-1} at grafting and disappearance at alkaline hydrolysis of the starch-PAN copolymer on the other hand resulted in the carboxylate and carboxamide bands in Figure 1c. The carboxylate group (–COONa) gave rise to two bands, a strong symmetrical stretching band at 1570 cm^{-1} and a weak symmetrical stretching band at 1440 cm^{-1} . These peaks are attributed to C=O stretching of the carboxamide functional groups, and the symmetric and asymmetric stretching modes of the carboxylate groups, respectively.

Results of heavy metal ions sorption by the grafted starch copolymer and hydrogel

Table 4 shows that all the sorption by the grafted starch copolymer and hydrogel for the metal ions are favourable, comparison of Freundlich isotherm constants obtained from other studies using other adsorbents shows that the values obtained in this study are comparable

(Salfuddin and Kumaran, 2005; Kadirvelu et al., 2001). Acid stripping with 2% HCl resulted in 99.6% metal recovery for the hydrogel and 52.2% for the grafted copolymer. This shows the ability of the product to be reused, upon drying between treatments.

DISCUSSION

Characteristics of the grafted copolymer and hydrogel

Several reaction variables were evaluated, that is, free-radical initiation, amount of acrylonitrile, and amount of sodium hydroxide, to determine grafting level and degree of saponification necessary to yield a high-capacity sorption material.

The characteristics of the grafted copolymer are as shown in Table 1. The results indicated that the CAN concentration of 20 mmol/l is sufficient for enhancement in the graft yield%, graft efficiency%, and the add-on% of graft copolymer. These may be explained in terms of the mechanism of ceric ion initiation which involve the formation of chelate complex that decomposes to generate free radical active sites on the starch polymer backbone (Athawale and Rathi, 1999). At the ceric ion concentration, the active sites on the starch polymer backbone at which the monomer can be grafted increase and these active free radicals in the presence of monomer generate graft copolymers (Nakason et al., 2004). The average number of grafting sites per backbone molecule depends on the concentration of the ceric ion and the substrate (Pourjavadi and Zohuriaan-Mehr, 2002; Zohuriaan-Mehr, and Pourjavadi, 2003), and reactivity of the monomer towards graft copolymer formation which follow the same order as observed for the dependence of graft level on monomer concentration (Okieimen and Ogbeifun, 1996). The results of the percent graft levels and graft efficiencies shows that graft copolymers formation is most likely due to combination of growing homopolymer chains with the radicals formed on the substrate (Ogbeifun and Okieimen, 2009). It has been reported however, that CAN concentrations beyond 20 mmol causes a decrease in both graft yield % and the add-on% of the copolymer while increasing the polymer. The decrease may be attributed to the solubility limitation of the starch at high CAN concentration. It may also be due to the termination of the growing grafted chains by excess ceric ions. It has been established that the extent of graft copolymer formation depend on the amount of monomer complexed. The increase in grafting percentage coupled with the increase monomer conversion may probably be due to increasing supply of monomer to starch macroradicals and the electronic charge of the monomer (Okieimen and Ogbeifun, 1996).

Structural aspects of the polymeric backbone are important factors affecting metal ions sorption. The prepared grafted cellulose copolymer is capable of

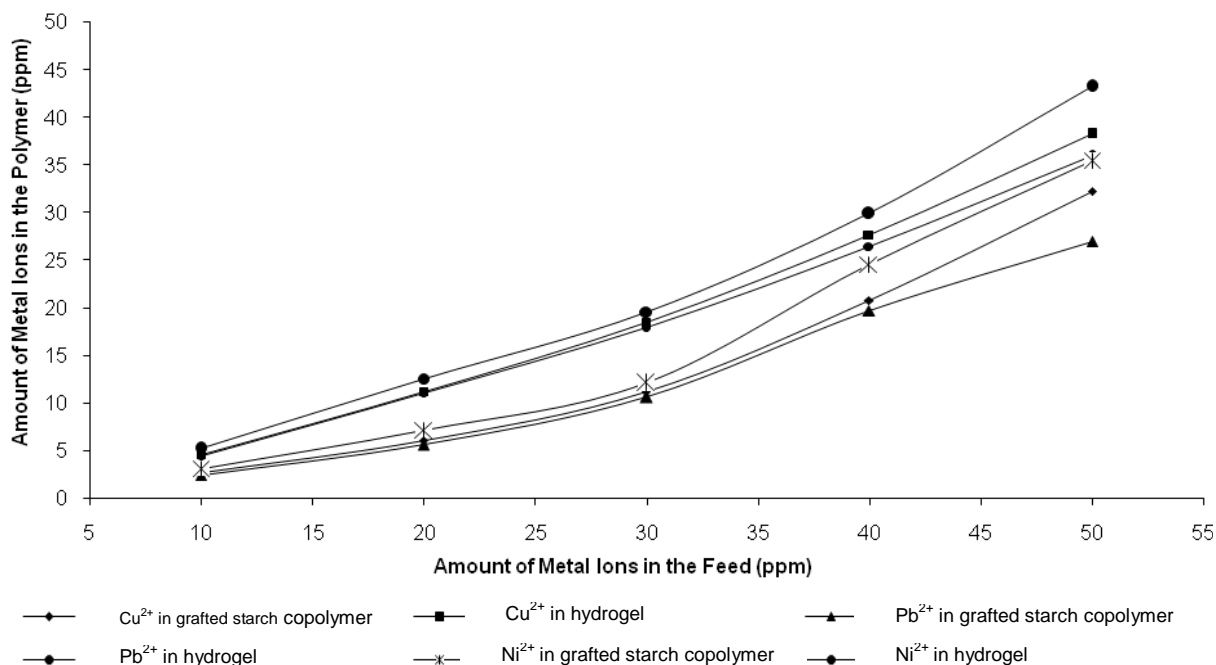


Figure 2. Comparison of the heavy metal ions Uptake by the grafted copolymer and the hydrogel.

removing metal ions both by adsorption on nitrogen of the amide groups and also by sorption in the bulk of hydrogel (Figure 2). Therefore, the structure of a polymeric hydrogel affects the level of polymer interaction with water and the provision of active sites to absorb or coordinate metal ions (Nayak and Singh, 2001; Yan Zheng et al., 2010). Saponification converts the same grafted poly (AN) chain and homopoly (AN) chain with cyano group (-C=N) as the main group to both amide (-CONH₂) and carboxylate (-COONa) groups. The nitrile groups of PAN were converted to a mixture of hydrophilic carboxamide and carboxylate groups during alkaline hydrolysis, which further enhances sorption of the metal ions.

Hence the sorption behavior and the quantity of metal ions taken up depend, in addition to the attributes of metal ions (ionic sizes, electropositivity, reactivity), also on different structural aspects of the polymer. It is clear from Tables 2 and 3, that the metal ions uptake percentage and retention capacity of Ni were higher than that of Cu and Pb. The equilibrium data yielded the following ultimate capacity values for the sorbent of the grafted copolymer: 54 mgPb/g, 64.5 mgCu/g, and 71.1 mgNi/g and for the hydrogel: 72 mgPb/g, 76.6 mgCu/g and 86.5 mgNi/g. Hydrolysis increases the sorption affinity of grafted copolymer toward metal ions. This can be attributed to the fact that the Ni ion has a lower atomic radius than other metal ions and consequently its sorption by polymer is high. In general, the amount of metal ions uptake by ion exchanger is affected by the electronegativity and hydrated values of metal ions. The sequence of metal ions sorption was as follows: Ni > Cu

> Pb.

To examine the relationship between sorbed (q) and aqueous concentration C at equilibrium, sorption isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich equations are most widely used. The isotherms were fitted to both the Freundlich and Langmuir adsorption models using the linear equations: The Freundlich equation is an empirical equation based on sorption on a heterogeneous surface (Salfuddin and Kumaran, 2005). The equation is commonly represented by:

$$q = aC^{1/b} \quad (6)$$

where a and b are the Freundlich constants characteristics of the system, indicating the sorption capacity and the sorption intensity, respectively.

To simplify the derivation of a and b , above equation can be linearized as:

$$\ln q = \ln a + (1/b) \ln C \quad (7)$$

Therefore, a plot of $\ln q$ versus $\ln C$ enables the constant a and exponent b to be determined. The Langmuir and Freundlich equations were used to describe the data derived from the sorption of Ni, Pb and Cu ions by the hydrogel over the entire concentration range studied. The plot of $\ln q$ versus $\ln C$ in Figure 3, showed that the experimental data reasonably well fitted the linearized equation of the Freundlich isotherm over the whole Ni, Pb, and Cu ions concentration range studied. Linear regression analysis was applied to each set of data

Table 2. Extent of heavy metal ions uptake by the grafted copolymer.

Metal ions for sorption	Metal ions in feed (ppm)	Metal ions in the polymer (ppm)	Metal ions uptake (%)	Retention Capacity (ppm/g)
Pb (II)	10	2.51±0.05	25.1±4.0	5.02±0.02
	20	5.67±0.03	28.4±1.0	11.3±0.02
	30	10.63±0.01	35.4±2.7	21.3±0.04
	40	19.71±0.06	49.3±2.5	39.4±0.08
	50	27.03±0.02	54.1±2.0	54.1±0.02
Cu (II)	10	2.78±0.05	27.8±1.6	5.56±0.02
	20	6.11±0.05	30.55±1.5	12.22±0.04
	30	11.18±0.02	37.25±2.1	22.36±0.02
	40	20.83±0.02	52.08±1.1	41.66±0.02
	50	32.26±0.02	64.52±1.5	64.52±0.04
Ni (II)	10	3.19±0.04	31.94±1.0	6.38±0.04
	20	7.23±0.16	36.14±2.5	14.46±0.30
	30	12.11±0.25	40.38±2.2	24.22±0.42
	40	24.61±0.05	61.52±1.5	49.22±0.06
	50	35.53±0.02	71.06±2.0	71.06±0.02

Table 3. Extent of heavy metal ions uptake by the native cassava starch hydrogel.

Metal ions for sorption	Metal ions in feed (ppm)	Metal ions in the polymer (ppm)	Metal ions uptake (%)	Retention Capacity (ppm/g)
Pb (II)	10	4.46±0.03	44.56±4.0	8.91±0.04
	20	11.03±0.01	55.16±1.0	22.06±0.02
	30	18.02±0.11	60.05±2.7	36.04±0.20
	40	26.43±0.05	66.08±2.5	52.86±0.10
	50	35.93±0.25	71.96±2.0	71.96±0.40
Cu (II)	10	4.67±0.05	46.77±0.4	9.35±0.02
	20	11.22±0.05	56.09±0.1	22.44±0.02
	30	18.57±0.01	61.89±0.7	37.14±0.01
	40	27.64±0.03	69.11±0.4	55.28±0.06
	50	38.28±0.02	76.55±0.1	76.56±0.02
Ni (II)	10	5.24±0.05	52.42±2.0	10.48±0.04
	20	12.56±0.02	62.81±1.0	25.12±0.04
	30	19.58±0.02	65.25±2.5	39.16±0.04
	40	29.94±0.05	74.85±2.0	59.80±0.10
	50	43.25±0.01	86.50±2.1	86.50±0.02

points and a correlation coefficient (r^2) and a probability value (p) representing the “goodness of fit” of the Freundlich or Langmuir model to the data was obtained by the linear regression program. Linear plots of (q/C) versus C , the Langmuir isotherm did not fit well for the Ni, Pb and Cu ions sorption by the hydrogel. In this study, however, Freundlich isotherm has a better fitting model than Langmuir as the former have higher correlation

regression coefficient than the latter. Thus, indicating to the applicability of a hydrogel sorption of the Ni, Pb and Cu ions. According to Kadirvelu et al. (2001), the essential characteristics of Freundlich isotherm can be explained in terms of a dimensionless constant separation factor (R_L), define by:

$$R_L = 1 / (1 + bC) \quad (8)$$

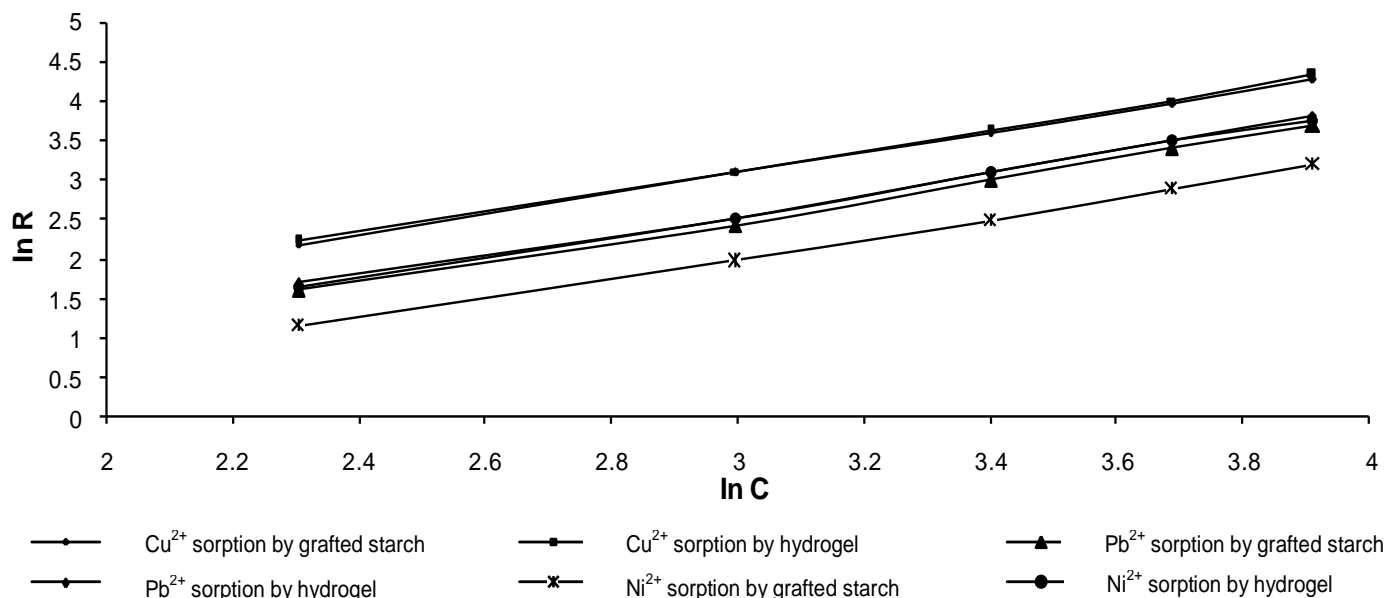


Figure 3. Freundlich isotherms for the comparison of heavy metal ions uptake by the grafted copolymer and the hydrogel.

Table 4. Isotherm model constants and correlation coefficients for sorption of metal ions from aqueous solution using the grafted starch copolymer and the hydrogel.

Metal ion	Sorbent type	a	b	R ²
Ni ²⁺	Starch copolymer	0.779	1.714	0.992
	Hydrogel	1.246	1.242	0.994
Cu ²⁺	Starch copolymer	0.646	1.330	0.994
	Hydrogel	1.221	1.390	0.994
Pb ²⁺	Starch copolymer	0.497	0.501	0.992
	Hydrogel	1.105	1.390	0.994

Where b is the Freundlich constant (sorption intensity) and C is the initial concentration of metal ion.

The value of R_L indicated the type of Freundlich isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$). In order to characterize metal ion sorption, either the Langmuir or Freundlich adsorption models are normally applied to adsorption systems such as described in Figures 2 and 3. Since the Langmuir model represents the formation of a monomolecular layer on the surface of the sorbent, this model would not be applicable to explain the isotherms in Figures 2 and 3. Since surface coverage does not appear to be complete (lack of surface saturation) for the hydrogels in Tables 2 and 3, the Langmuir model may not be the best choice because it is normally used to describe systems in which sorption site saturation occurs.

When the Langmuir model was applied to the data in Tables 2 and 3, the adsorption constants, K_a and Q , generally had “ p ” values < 0.05 , which meant their significance was in doubt (data not shown). In contrast, the Freundlich model describes low and intermediate surface coverage of the sorbent and is more forgiving than the Langmuir model in describing the exact nature of the coverage, be it monolayer or multilayer. Therefore, we applied the Freundlich model to the isotherms in Tables 2 and 3 and obtained the linear representations shown in Figures 2 and 3. Freundlich constants were obtained from these lines and the values are given in Table 4. All of the linear representations in Figure 3 had high correlation coefficients (r^2) and the fact that $p < 0.01$ in all cases, indicates that the Freundlich model adequately represents the data, this corroborates the results of the investigation conducted by Pınar et al. (2007).

Conclusions

It has been shown that the use of native cassava starch grafted poly (acrylonitrile) for heavy metal ions removal is technically feasible, eco-friendly and with high efficiency. Besides that, being composed of natural polysaccharides, it helps in reduction of environmental pollution and safe disposal of heavy metals, being biodegradable. This sorbent is a good candidate for sorption of not only heavy metal ions but also other organics in waste water stream. Grafting enhances metal ions uptake from aqueous media and the extent of uptake is influenced by the sizes of the ions. These results are of interest to the development of hydrogel-based technologies for water purification and metal ions separation and enrichment.

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