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Removal of heavy metals from aqueous media using native cassava starch-poly (sodium acrylate-co-acrylamide) hydrogel

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ABSTRACT

Native cassava starch poly(sodium acrylate–co-acrylamide) hydrogel was synthesized in aqueous solution by physical mixture. Saponification of the mixture was done by reaction with sodium hydroxide. The reaction was confirmed using infrared spectrophotometer and scanning electron microscope. The hydrogel was used as sorbent for the uptake of selected heavy metals from the aqueous media. The sorption capacity was evaluated by measuring the extent of sorption of chromium, copper, and lead metals ions, under equilibrium conditions, and verified using the Freundlich isotherm model. The equilibrium data yielded the following ultimate capacity values for the hydrogel: 76.6% Pb, 72.0% Cu and 2.8% Cr. Hydrolysis increases the sorption affinity of hydrogel toward metal ions.

KEYWORDS

Polymer gels;
Hydrogel;
Heavy metals;
Sorption.

INTRODUCTION

Many environmental studies have revealed widespread contamination of water by different chemicals used in the chemical industry during manufacturing process[1]. These chemicals include organic compounds, heavy metals and other pigments like dyes in the textile industry. At least 20 metals are classified as toxic and half of these are emitted into the environment in quantities that pose risks to human health[2]. Some of these constitute the major source of contaminants in portable water supply to humans and livestock. These chemicals find their way into ground water, which cause pollution and could impair plant growth and result to a great risk to human health and the environment[2,3]. Efficient removal of these pollutants from the environment is still a problem.

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[4-6]. 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 attrative 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[7]; Ni[8]; Cr[9]; Cu[10]. 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.

Since polysaccharides are abundant from renewable inexpensive, safe (non-toxic) and amenable to both chemical and biochemical modifications. It is not surprising that they find widespread and extensive use. Hydrogel by physical mixture is a unique method among the techniques for modifying natural polymers mostly polysaccharides. Polysaccharides hydrogel have been prepared in order to add new properties to the natural polymer with a minimum loss of native properties[11].

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.

The present communication is an attempt to evaluate the equilibrium sorption properties of Nigeria grown native cassava starch-poly(sodium acrylate –co-acrylamide) hydrogel. The combination of the useful properties of polyacrylonitrile and that of natural cassava starch, could introduce a modified biosorbent matrix with many applications and superior sorption capabilities.

MATERIALS AND METHODS

Materials

Cassava starch was sourced from a local cassava starch processing factory in Benin City, Nigeria. Polyacrylonitrile (PAN) was synthesized through a method mentioned in the literature[12]. Double distilled water was used for the hydrogel preparation and swelling measurements. Chemicals used were of analytical grade and were supplied by the British Drug House (B.D.H), England.

Hydrogel preparation

The procedure for alkaline hydrolysis of starch-PAN mixture was conducted as follows. Starch solution was prepared in a 1-l reactor equipped with mechanical stirrer and gas inlet. In a typical reaction: 1g Starch was dissolved in 30.0 ml of distillated degassed water containing 1wt.% of acetic acid solution. After complete dissolution of starch, 1.0 weight percent of sodium hydroxide was added to the solution at 90 °C. The mixture was allowed to stir for 120 min. The 1.5g polyacrylonitrile was dispersed in the reaction mixture to saponify for 3h at 95°C. During the saponification, NH_3 gas was evolved and a color change from red to light yellow. This discoloration was an indication of the reaction completion. The pasty mixture was allowed to cool to room temperature and neutralized to pH 8.0 by addition of 10 wt % aqueous acetic acid solution. Then, the gelled product was scissored to small pieces and poured in 200ml ethanol to dewater for 5 h. The hardened particles were filtered and dried in oven at 50 °C, for 10 h. After grinding, the powdered superabsorbent hydrogel was stored away from moisture, heat and light. Hydrogel formation was confirmed on a Nicolet impact 410 FTIR spectrophotometer using a KBr pellet and the hydrogel surface morphology was examined using scanning electron microscope (SEM).

Swelling measurements using tea bag method

The tea bag containing an accurately weighed powdered sample (0.5 ± 0.001 g) with average particle sizes of 350μm mesh was immersed entirely in 200ml distilled water and allowed to soak for 3 h at room temperature. The tea bag was hung up for 15 min in order to remove the excess fluid. The Water retention value (WRV) was measured twice using the following equation:

$$\textbf{Water retention value } (g/g) = \frac{(W_2 - W_1)}{W_1} \qquad (1)$$

Where, W_2 and W_1 are the weights of water swollen hydrogel and dry hydrogel in grams, respectively

Equilibrium uptake of Heavy metal ions from aqueous media

Batch equilibrium experiments were carried out using the 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 0.5g of hydrogel for 30mins in 100ml aqueous media containing varying concentrations of ions of (Lead, Copper, and Chromium) respectively[13-15].

Lead Nitrate $(PbNO_3)_2$, Copper Sulphate $(CuSO_4)$, Potassium Dichromate $(K_2Cr_2O_7)$ were used as the source of Lead (II), Copper (II), and Chromium (VI) ions for the aqueous media. The Pb, Cu, and Cr stock solutions were prepared by dissolving 80mg of $Pb(NO_3)_2$, 124mg of $CuSO_4$, and 131mg of $K_2Cr_2O_7$ in 1000ml of deionized water respectively.

The change in Pb(II), Cu(II), and Cr(VI) concentrations due to sorption was determined by AAS after filtration.

The extent of uptake and retention capacity of the hydrogel are expressed in percentage as follows[16]:

$$\text{Metal ions uptake\%} = \frac{\text{amount of metal in polymer}}{\text{amount of the metal in the feed}} \times 100 \qquad (2)$$

$$\text{Metal ions retention} = \frac{\text{amount of metal ions in polymer}}{\text{weight of dry polymer}} \qquad (3)$$

Results are as presented in TABLE 2

TABLE 1 : Characteristics of the hydrogel

Characteristics	Results
Colour	White
Water retention value (g/g)	382
Toxicity	No
Water Soluble	No
Dimension (μm)	150-350
Density (g/cm^3)	1.5
pH	8.0

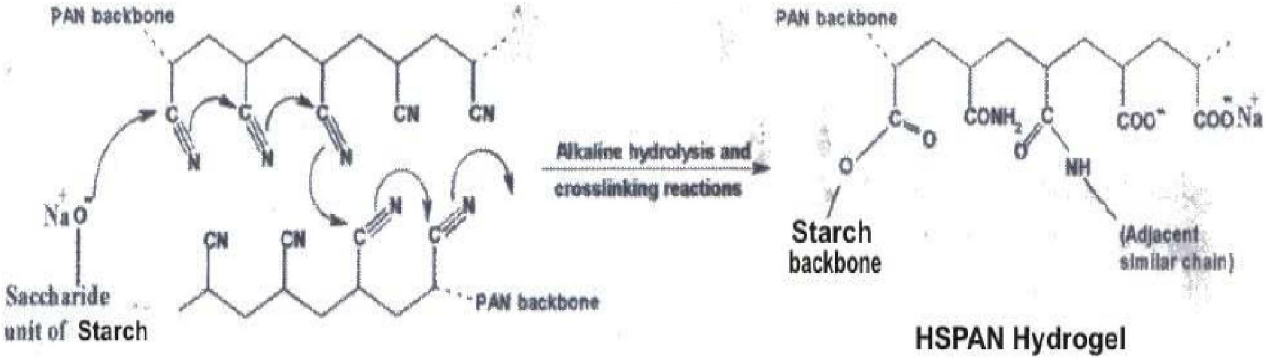
TABLE 2 : Extent of heavy metal uptake by the hydrogel

Metal ions for sorption	Metal ions in feed (ppm)	Metal ions in the polymer (ppm)	Metal ions uptake (%)	Retention Capacity (ppm/g)
Cu(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
Pb (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
Cr (VI)	10	0.24±0.005	2.42±0.2	4.82±0.04
	20	0.56±0.002	2.81±0.1	5.62±0.04
	30	0.58±0.002	1.93±0.25	3.86±0.04
	40	0.94±0.005	1.35±0.20	2.70±0.10
	50	0.25±0.001	0.50±0.21	1.00±0.02

RESULTS AND DISCUSSION

Mechanism of hydrogel formation

The reaction mechanism for hydrogel synthesis is shown in Scheme 1. The hydroxyl groups of starch substrate was converted to corresponding alkoxide ions using sodium hydroxide solution. Then, these macroalkoxides initiate crosslinking reaction between some adjacent polyacrylonitrile pendant chains. This reaction leads to intermediate formation of naphthyridine cyclic structures (including imine, -C=N-, conjugated bonds) with deep red color. The intermediate was then hydrolyzed using residual sodium hydroxide aqueous solution to produce hydrophilic carboxamide and carboxylate groups with a resulting color change from red to light yellow. This sharp color change was used as an indication to halt the alkaline treatment.



Scheme 1 : Proposed mechanism for crosslinking during hydrolysis of the nitrile groups of the hydrolyzed starch-polyacrylonitrile (HSPAN) mixture to produce the hydrogel.

Maximum swelling capacity of 382g/g was obtained in water. It has been stated that swelling capacity of hydrogels is influence by the pH, hydrolysis time, temperature and the medium[17]

Infrared analysis

Infrared spectroscopy was carried out to confirm the chemical structure of the hydrogel. Figure 1 shows the FTIR spectra of the physical mixture and the resulted hydrogel, St-PAN. The band observed at 2242 cm^{-1} can be attributed to stretching of –Ca”N group of PAN (Figure 1a). The hydrogel comprise a starch backbone with side chains that carry carboxamide and carboxylate functional groups that are evidenced by three new peaks at 1452, 1156, and 1675 cm^{-1} (Figure 1b). These peaks are attributed to C=O stretching in carboxamide functional groups and symmetric and asymmetric stretching modes of carboxylate groups, respectively[16,17]. As shown in Scheme 1. and Figure 1b, after alkaline hydrolysis, most of the nitrile groups are converted to carboxamide and carboxylate groups.

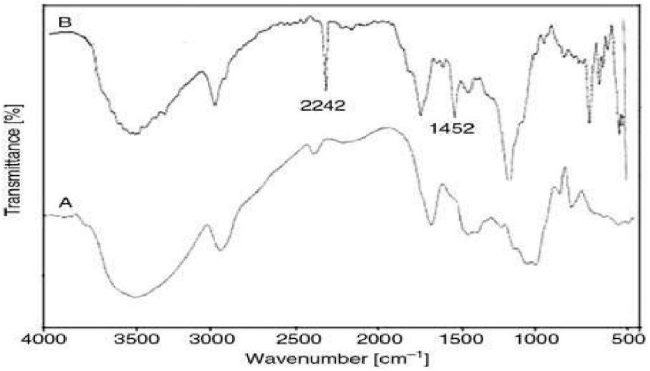


Figure 1 : FTIR spectra of (A) starch and (B) the cross linked hydrogel.

Hydrogel morphology

The surfaces of the starch and the hydrogel were observed with the scanning electron microacope (SEM). Figure 2 shows the picture of the starch and figure 3 shows the picture of the hydrogel. From the figures it is obvious that the hydrogel has a porous structure, unlike the starch. The pores are the regions of water permeation and interactions sites of external stimuli with the hydrophilic groups of the copolymers. SEM picture of the starch (Figure 2), clearly shows change in the surface topology of the starch after reaction due to the growing Polyacrylonitrile chain.

Results of heavy metal ions sorption by the hydrogel

Structural aspects of the polymeric backbone are important factors affecting metal ions sorption. The prepared hydrogel removes metal ions both by adsorption on nitrogen of the amide groups and also by sorption in the bulk of hydrogel as shown in the Figures 2 and 3. Therefore, the structure of a polymeric hydrogel affects the level of polymer interaction with water and the provision of active sites to absorb coordinate metal ions[13,14].

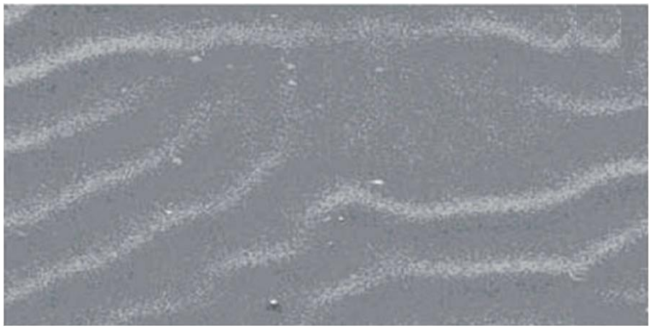


Figure 2 : Scanning electron microscope picture of the native cassava starch

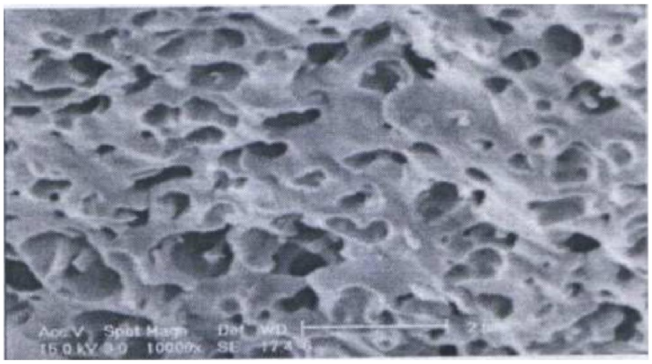


Figure 3 : Scanning electron microscope picture of the hydrogel.

Hence the sorption behaviour 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 TABLE 2 and Figure 3 that the metal ions uptake percentage and retention capacity of Cr were far lower than Cu and Pb. This can be attributed to the fact that the Cr ion has a higher oxidation state than other metal ions and consequently its sorption by polymer at that state is very low. 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: Pb > Cu > Cr.

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 Freundlich equation is an empirical equation based on sorption on a heterogeneous surface. The equation is commonly represented by:

$$q = aC^{1/b} \qquad (4)$$

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:

$$\mathrm{Inq} = \mathrm{Ina} + (1/b)\,\mathrm{InC} \qquad (5)$$

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 Cr, Pb and Cu ions by the hydrogel over the entire concentration range studied. The plot of *Inq* versus In*C* in Figure 4 showed that the experimental data reasonably well fitted the linearized equation of the Freundlich isotherm over the whole Pb and Cu ions concentration range studied with the exception of the Cr ions which did not fit the Freundlich isotherm. Linear plots of ln (C/q) versus ln C, Figure 5 showed that the Langmuir isotherm did not fit well for the Cr, 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 Pb and Cu ions.

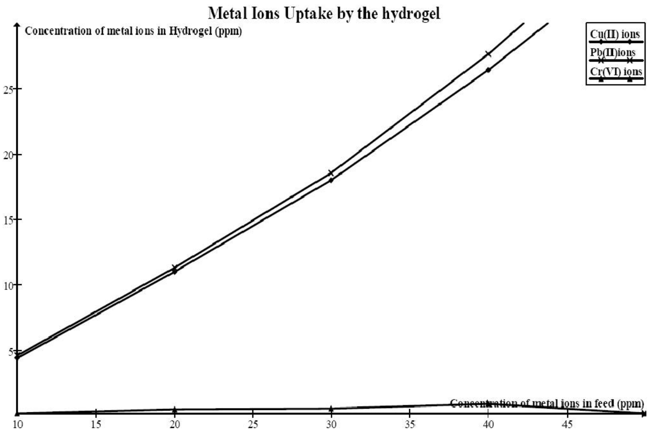


Figure 4 : Metal ions uptake by the hydrogel

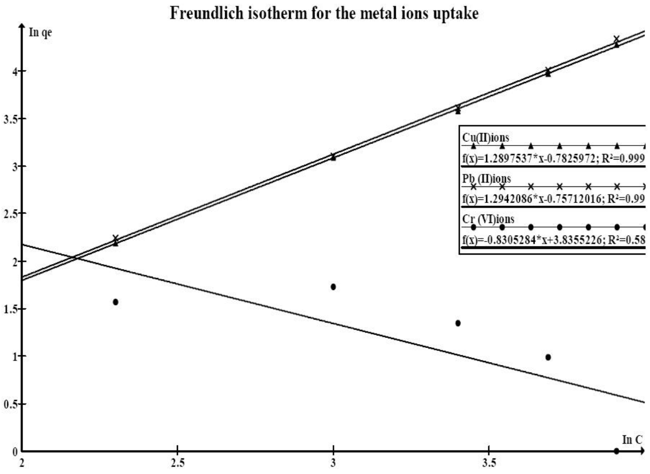


Figure 5 : Freundlich isotherm for the metal ions uptake by the hydrogel

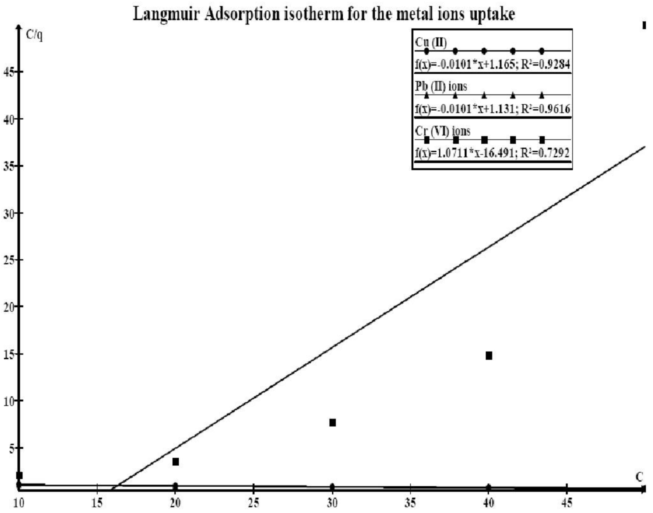


Figure 6 : Langmuir isotherm for the metal ions uptake by the hydrogel

CONCLUSION

It has been shown that the use of native cassava starch- poly(sodium acrylate-co-acrylamide) hydrogel for heavy metal ions removal is technically feasible, eco-friendly and with high efficiency. Besides that, being composed of natural polysaccharides and biodegradable, it helps in reduction of environmental pollution and safe disposal of heavy metals. This sorbent can be a good candidate for sorption of not only heavy metal ions but also other organics in waste water stream.

Porosity and anions on the surface of the hydrogel enhances metal ions uptake from aqueous media and the extent of uptake is influenced by the sizes and state of the ions. These results are of interest to the development of hydrogel-based technologies for water purification and metal ions separation and enrichment in Nigeria.

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