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Sorption of Some Heavy Metal Ions by Chitosan and Chemically Modified Chitosan

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Abstract. Chitosan was produced by deacetylation of chitin with sodium hydroxide at a temperature of 117 °C (Randal *et al*, 1979). In this study, chitosan was prepared from African giant land snail (*Archachatina marginata*), and acrylamide was grafted onto the chitosan to produce chitosan grafted acrylamide (cga). The two varieties (chitosan and cga) were separately used as adsorbents for the removal of some heavy metal ions (Pb^{2+}, Cd^{2+}, and Ni^{2+}) from aqueous systems. The amount of metal ions (Pb^{2+}, Cd^{2+}, and Ni^{2+}) adsorbed onto chitosan at optimum temperature (45 °C) ranged from 43.88-60.60 %, 27.50-58.60% and 41.30-58.90%, respectively. That adsorbed onto cga ranged from 49.40-65.56%, 56.50-97.90% and 29.60-64.80%, respectively. Results revealed that cga sorption capacity was approximately twice as high as chitosan.

Keywords: heavy metals, sorption, chitosan, metal ions

Introduction

Industrial revolution has accelerated the release of pollutants into the environment. Among these, heavy metals like Hg, Pb, Cd, Ni, As, and Sn, are important pollutants that are highly toxic to humans and other living organisms. Hence their presence in surface and underground waters above the limit is highly undesirable (Ricordel *et al*, 2001; Miroslav and Vladimir, 1999; Jackson and Jackson, 1996; Manahan, 1994).

Removal of heavy metals from water is important to protect public health. Natural processes can no longer clean, the environment of the enormous quantities of pollutants that are generated daily. Usually, treatement at source is the only practical means of controlling toxic metal pollution (Miroslav and Vladimir, 1999). Waste waters containing toxic metals may be treated by addition of anions that cause the precipitation of the metals as insoluble salts (Jackson and Jackson, 1996), while other methods include membrane filtration, activated carbon adsorption and co-precipitation/adsorption. Ion-exchange resins may also be used to treat industrial effluents.

These processes are efficient but expensive. To develop cheaper methods of industrial effluent treatments, Okolo and Okuo, 2004; Okuo and Ozioko, 2001, had used treated periwinkle shell, coconut husk/shell, and palm kernel fibre, to remove Pb^{2+}, Hg^{2+}, and Cd^{2+} ions from aqueous systems. Reduction in the cost of industrial effluent treatments by devising cheap and affordable alternatives is highly desirable. This will contribute, to minimize the toxic effects of the heavy metals. This paper is aimed at investigating the readily available and cheap raw materials such as snail shell (which is the source of chitosan) for possible applications in isolating some toxic metals from certain industrial wastes. This would not only solve the problem of littering the environment with these raw materials but also to get a better utilization of them.

Materials and Methods

Chemicals and reagents. Analar grade acetic acid, ether, ethanol, sodium hydroxide, cadmium sulphate, lead nitrate, nickel nitrate, ethylenediamminetetraacetic acid (EDTA), hexamethylene tetraamine, sulphuric acid, nitric acid, magnesium sulphate, xylenol orange, eriochrome black T, potassium peroxidisulphate, acetone and quinol, were procurred from BDH.

Preparation of chitosan. Chitin material from African gaint snail shell (*Archachatina marginata*) was used. 25.0 g of powder prepared by grinding dried snail shell (bought from a local market in Benin City, Nigeria) was heated with 1.2 litre of 40% aqueous sodium hydroxide solution at 117 °C for a period of 180 min. The mixture was allowed to cool and then filtered and washed with distilled water. It was air-dried and weighed. This gave an impure chitosan. This was purified by dispersing it in 500 ml of 10% aqueous acetic acid. The mixture was centrifuged after 24 h. A clear supernatant liquid was obtained and treated with dropwise addition of 40% aqueous sodium hydroxide solution until a white flocculant precipitate was formed at pH 6.8. This was recovered by centrifugation. It was washed repeatedly with distilled water, ether, ethanol, respectively and allowed to dry. The product formed was

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*Author for correspondence; E-mail: okuojm@yahoo.com taken as pure chitosan because it was dissolved in acidic media. Chitosan is soluble in aqueous acidic solutions of certain concentrations (Randal *et al*,1979). For example, it is soluble in 1-5% H_2SO_4 and in 0.5-10% acetic acid but insoluble in 0.5% and above 7.5% H_2SO_4.

Preparation of metal ion solutions. Solutions of Pb^{2+}, Cd^{2+}, and Ni^{2+} were prepared at varying concentrations of 50, 100, 200, 400, and 500 mgl^{-1} for each metal ion. The pH of all solutions was at near neutrality (6.5-7.5). 100 ml portion of each solution was used for sorption experiments.

Grafting method. Grafting co-polymerization, which can be carried out on pre-existing polymers (natural or synthetic) has the advantage of incorporating properties such as elasticity, sorbancy, ion-exchange capabilities, thermal resistance, and resistance to microbial attacks onto a polymer (Matjevic and Stryker, 1966). Grafting modifies both physical and chemical properties of the polymer. The grafting procedures employed was based on the method of Lepoutre and Hui, (1975). The chitosan grafted with acrylamide or otherwise referred to as cga in this paper.

Adsorption of metal ions on the chitosan and chitosan grafted acrylamide (cga). The uptake of lead, cadmium and nickel ions on the chitosan and the cga was determined by equilibrium sorption studies using complexometric titrations involving EDTA (Vogel, 1961).

Equilibrium sorption of metal ions on chitosan and cga. Equilibrium sorption of metal ions was done by shaking the adsorbent (1.0 g) with 100 ml of each metal ion solution, whose concentration had previously been determined. At the end of the contact period of 40 min, the mixture was filtered and the residual concentration of the metal ion determined by EDTA complexometric titrations at various temperatures. Titration was done in triplicates for each metal ion, and average titre values calculated.

The difference between the initial and residual metal ion concentrations was obtained as the amount of metal ion bounded by the chitosan and cga, making corrections for the volume of metal ion solution encapsulated by the substrate. The uptake level of metal ions as a function of the concentration of the metal ions was also studied.

Results and Discussion

The effect of temperature on the sorption of metal ions from solution by chitosan are presented in Tables 1-3. Table 4 and 5 shows the removal of metal ions from solution by cga at optimum temperature (45 °C).

Tables 1-3 show that the optimum temperature for adsorption of metal ions onto untreated chitosan is 45 °C. It was observed that adsorption increases from 30-45 °C. As temperature is raised from 30 °C, it is likely to enhance the interaction between the active sites and the metal ions, and consequently increasing the rate of metal ions uptake (Okolo and Okuo, 2004; Okuo and Ozioko, 2001).

However, there was a sharp drop in the rate of metal ions uptake when the temperature was increased to 60 °C. This higher temperature raises the kinetic energy of the system, thereby energizing the substrate metal ion complex molecules. This leads to instability of substrate metal ion complex. All these might be responsible for desorption observed at 60 °C. It is also possible that some of the weakly bonded groups may have been lost at higher temperature. The chitosan grafted with acrylamide, cga, has a higher adsorption capacity than untreated chitosan. For example, the amount of Pb^{2+} ions adsorbed onto untreated chitosan at room temperature (45 °C)

Table 1. Effect of temperature on sorption of Pb^{2+} ion by chitosan

Initial concentration (mg/100 ml) of Pb^{2+}	Equilibrium concentration (mg/100 ml)			Amount adsorbed (mg/100 ml)			D = loga_e/log c_e			Percentage retention		
	30 °C	45 °C	60 °C	30 °C	45 °C	60 °C	30 °C	45 °C	60 °C	30 °C	45 °C	60 °C
20	13.48	7.88	12.60	6.53	12.12	7.40	0.72	1.20	0.79	32.70	60.60	37.00
40	32.60	22.48	31.47	7.40	17.52	8.53	0.58	0.92	0.62	18.50	43.88	21.00
80	60.70	37.09	44.96	19.30	42.91	35.04	0.72	1.04	0.92	24.13	53.36	43.80
120	67.44	53.95	61.82	52.56	66.05	58.18	0.94	1.05	0.98	43.80	55.04	48.48
160	89.92	73.06	76.43	70.08	86.94	83.57	0.95	1.04	1.02	43.80	54.34	52.23
200	107.60	87.67	92.17	92.40	112.38	107.83	0.87	1.06	1.04	46.20	56.19	53.92

D = distribution coefficient; a_e = equilibrium sorption; c_e = equilibrium concentration of the metal ion

Table 2. Effect of temperature on sorption of Cd^{2+} ion by chitosan

Initial concentration (mg/100 ml) of Cd^{2+}	Equilibrium concentration (mg/100 ml)			Amount adsorbed (mg/100 ml)			D = $\log a_e/\log c_e$			Percentage retention		
	30 °C	45 °C	60 °C	30 °C	45ºC	60 °C	30 °C	45 °C	60 °C	30 °C	45 °C	45 °C
20	15.80	8.20	10.36	4.20	11.72	9.64	0.52	1.18	0.96	21.00	58.60	48.20
40	31.08	29.00	29.84	8.92	11.00	10.16	0.64	0.71	0.69	22.30	27.50	25.40
80	49.72	41.80	66.32	30.28	38.80	13.68	0.87	0.98	0.63	37.85	48.50	17.10
120	66.32	53.88	89.12	53.68	66.12	30.88	0.95	1.05	0.76	44.73	55.10	25.73
160	91.16	72.52	116.00	68.84	87.48	44.00	0.94	1.04	0.80	43.03	54.68	27.50
200	116.00	87.04	130.00	84.00	112.96	70.00	0.93	0.97	0.88	42.00	56.48	35.00

D = distribution coefficient; a_e = equilibrium sorption; c_e = equilibrium concentration of the metal ion

Table 3. Effect of temperature on sorption of Ni^{2+} ion by chitosan

Initial concentration (mg/100 ml) of Ni^{2+}	Equilibrium concentration (mg/100 ml)			Amount adsorbed (mg/100 ml)			D = $\log a_e/\log c_e$			Percentage retention		
	30 °C	45 °C	60 °C	30 °C	45 °C	60 °C	30 °C	45 °C	60 °C	30 °C	45 °C	60 °C
20	14.08	8.22	11.74	5.92	11.78	8.26	0.68	1.18	0.86	29.60	58.90	41.30
40	30.53	23.48	28.18	9.47	16.52	11.82	0.66	0.89	0.74	31.10	41.30	29.53
60	46.97	34.05	3.44	13.03	25.95	16.56	0.66	0.92	2.26	21.72	43.25	27.60
80	54.01	44.62	51.66	25.99	35.38	28.34	0.82	0.94	0.85	32.49	44.23	35.43

D = distribution coefficient; a_e = equilibrium sorption; c_e = equilibrium concentration of the metal ion

Table 4 . Sorption of $Pb^{2+}$and Cd^{2+} ions by cga at 45 °C.

Initial concentration (mg/100 ml) of metal ion^{+}	Equilibrium concentration (mg/100 ml)		Amount adsorbed (mg/100 ml)		D = $\log a_e/\log c_e$		Percentage retention	
	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}
20	7.64	0.42	12.36	19.58	1.24	- 3.39	61.80	97.90
40	20.24	14.92	19.76	25.08	0.99	1.20	49.40	62.70
80	33.28	34.81	46.72	45.19	1.10	0.65	58.40	56.49
120	41.60	49.73	78.40	70.27	1.17	1.09	65.33	58.56
160	55.76	67.14	104.24	92.86	1.15	1.08	65.15	58.04
200	68.80	84.96	131.20	115.04	1.15	1.07	65.56	57.50

D = distribution coefficient; a_e = equilibrium sorption; c_e = equilibrium concentration of the metal ion

ranged 43.88-56.19% compared with that adsorbed onto cga: 49.4-65.56%. Similarly, for Cd^{2+} ions , untreated chitosan gave 27.50-58.60%, while cga yielded 56.49-97.90% (Tables 1 and 4 respectively).

The uptake levels of nickel ions at optimum temperature (45 °C) by untreated chitosan and cga differ from those observed for Pb^{2+} and Cd^{2+} ions. For instance, the amount of Ni^{2+} ions adsorbed using untreated chitosan and cga ranged between 41.30-58.90% and 29.6-64.8% respectively (Tables 3 and 5). This might be due to variations in the characteristics of the adsorbate, whose hydration energy and ionic size were 2.11 and 0.69, respectively, compared with that of lead: 1.48 and 1.26, and cadmium: 1.81 and 0.97 (Lee, 1999).

The higher adsorption capacity of cga for metal ions might be due to the introduction of carbonyl (C=O) and additional amino (NH_2) groups onto chitosan. The carbonyl and amide groups introduced during grafting are additional points of attachment that can enhance the adsorptive capacity of the substrate. Adsorption process can also be expressed in terms of distribution coefficient, D (Tables 1-3).

Table 5. Sorption of Ni^{2+} ion by cga at 45 °C

Initial concentration mg/100 ml of metal ion	Equilibrium concentration mg/100 ml	Amount, mg/100 ml adsorbed	D = log a_e/ log c_e	Percentage retention
20	7.04	12.96	1.31	64.8
40	23.95	16.05	0.88	40.13
60	39.69	20.31	0.82	33.65
80	56.36	23.64	0.78	29.55

From Tables 1- 5 and at 45 °C, the distribution coefficient, D of Pb^{2+} ion for chitosan and cga ranged between 0.92-1.20 and 0.99-1.24, respectively. That of Cd^{2+} ion ranged from 0.71-1.18 and -3.39-1.20 for chitosan and cga, respectively. Similarly, the values for Ni^{2+} ion ranged between 0.89-1.18 and 0.78-1.31 for chitosan and cga, respectively. These results show that there is slight variation of D with concentration of metal ions. The value of D is of practical significance in the treatment of heavy metal laden waste waters. Primarily, it allows the number of cycles of equilibrium sorption processes to be deduced. For instance, Cd^{2+} ions with distribution coefficient of -3,39 to 1.07 (Table 4) for the cga would be more easily removed from waste waters containing Pb^{2+}, Cd^{2+} and Ni^{2+} contaminants.

Figs. 1, 2 and 3 show the Freundlich isotherms for the adsorption of Cd^{2+}, Pb^{2+} and Ni^{2+} ions, respectively, on chitosan and cga. The Freundlich isotherm equation is given as:

$$a = KC^n$$

where 'a' is the equilibrium sorption, C is the equilibrium concentration of the metal ions, n and K are the exponent and coefficient of the isotherm equation, respectively. The equation can also be rendered into logarithmic terms, as:

$$\text{Log } a = \log K + n \log C.$$

A plot of log a against log C gives a linear plot with slope equals 1/n and intercepts on the log a axis allows for the

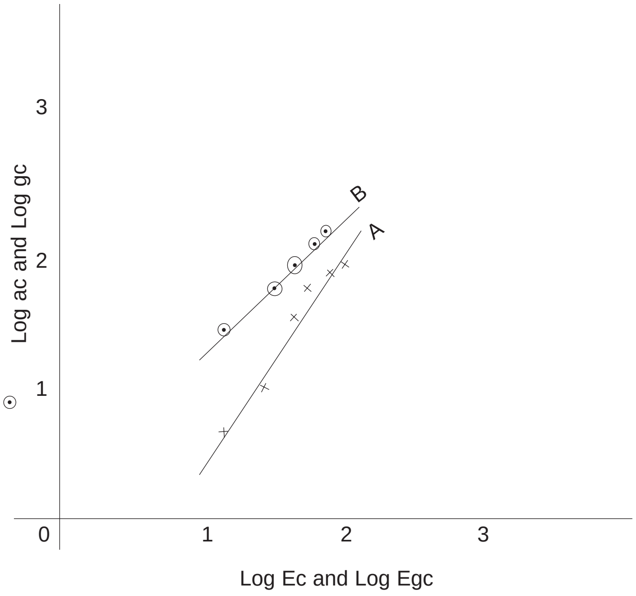

Fig. 1. Cd^{2+} ion uptake on chitosan and cga.
A = graph of log. ac vs log Ec;
B = graph of log. gc vs log Egc.
ac = amount of Cd^{2+} ion adsorbed per unit mass of chitosan;
Ec = equilibrium conc of Cd^{2+} ion after adsorption on chitosan;
gc = amount of Cd^{2+} ion adsorbed per unit mass of cga;
Egc = equilibrium conc of Cd^{2+} ion after adsorption on cga.

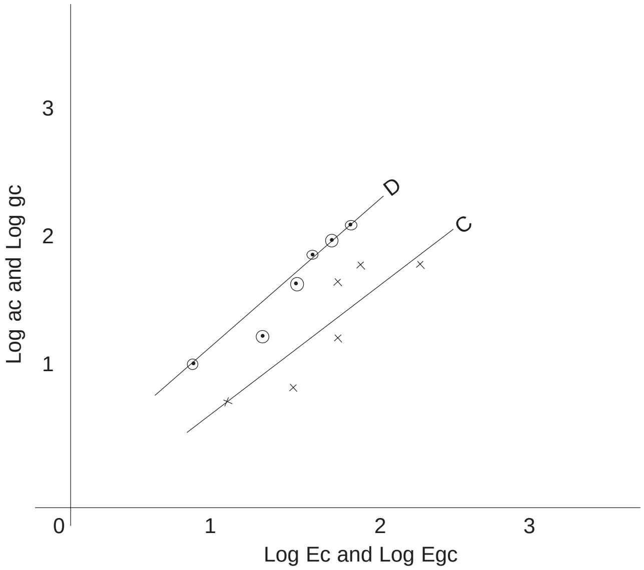

Fig. 2. Pb^{2+} ion uptake on chitosan and cga.
C = graph of log ac vs log Ec.
D = graph of log gc vs log Egc.
ac, Ec, gc, and Egc as in Fig. 1.

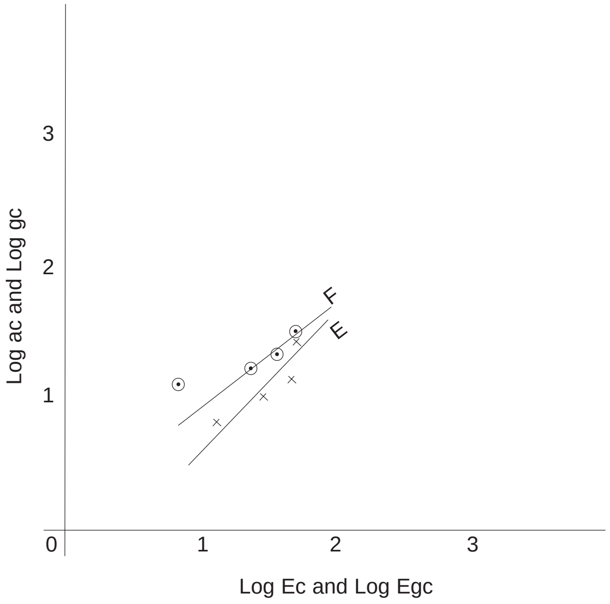

Fig. 3. Ni^{2+} ion uptake on chitosan and cga.
E = graph of log ac vs log Ec;
F = graph of log gc vs log Egc.
ac, Ec, gc and Egc as in Fig. 1.

estimation of K. Thus, the value of 'n' and 'K' were determined to be in the range of 0.5-0.63 mg/100ml for chitosan and 1.08- 1.16 mg/100ml for cga, with respect to Pb^{2+} ion. The value of 'n' shows the extent of adsorption of the metal (Pb^{2+}) ion. The exponent, n, of the Freundlich equation for Pb^{2+} ion sorption has a value close to unity and suggests a simple mechanim of sorption for the metal (Pb^{2+}) ion on the cellulosic material (chitosan). When the value of 'n' is much lower than unity, a complex mechanism is involved in adsorption (Chanda *et al*, 1983; Glasstone and Lewis, 1983). These values of 'n' indicate that the adsorption of lead ion is simple for cga because 'n' is close to unity, but complex for untreated chitosan. The mechanism for cadmium ion is complex for both chitosan and cga. This is because 'n' values are lower than unity.

Conclusion

This study shows that the deacetylation of chitin (snail shell) to chitosan may have great economic prospect in industry, especially in the treatment of industrial effluents containing heavy metals. The incorporation of acrylamide onto chitosan undeniably enhanced the sorption capacity. The equilibrium sorption data revealed that relatively large amount of sorption cycles using the adsorbent would be required in the treatment of heavy metalladen wastewaters. In addition, this study also shows that apart from nature of adsorbent, other factors such as metal ion concentration and temperature, also play a significant role in metal ion uptake.

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