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

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Abstract: In this study, chitosan was prepared from African giant land snail (*Archachatna marginata*) and acrylamide is grafted onto the chitosan to produce Chitosan Graft Acrylamide (CGA). The two varieties (chitosan and CGA) are 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 reveal that CGA sorption capacity is approximately twice as high as chitosan.

Key words: Heavy metals, sorption, chitosan, modified chitosan

INTRODUCTION

Nowadays, industrial revolution has accelerated the release of pollutants into the environment and heavy metals are among the most important pollutants in our environment. Many of the heavy metals, e.g., Hg, Pb, Cd, Ni, As and Sn are highly toxic to humans and other living organisms and their presence in surface and underground waters at above background concentrations is undesirable (Miroslav and Vladimir, 1999; Jackson and Jackson, 1996; Manahan, 1994; Ricordel *et al.*, 2001).

Removal of heavy metals from water is important to protect public health, as natural processes can no longer cleanse the environment of the enormous quantities of pollutants that are generated daily. Usually, treatment 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, 1976). 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 may be efficient but are expensive. Intending to develop cheaper methods of industrial-effluent treatments, Okuo and Ozioko (2001) and Okolo and Okuo (2004), 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. Recently Okuo *et al.*, (2006) and Okuo and Okolo (2006), used pre-treated Nigerian fresh water algae and blended periwinkle shell to selective remove heavy metal ions from aqueous solutions containing mixed metal ions. Reduction in the cost of industrial-effluent treatments by devising cheap and affordable alternatives is highly desirable. This will contribute, in no small measure, to minimizing poisoning by these toxic metals. This study 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 get them to be gainfully applied.

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MATERIALS AND METHODS

Chemicals and Reagents

Analar grade acetic acid, ether, ethanol, sodium hydroxide, cadmium sulphate, lead nitrate, nickel nitrate, Ethylenediaminetetraacetic Acid (EDTA), hexamethylene tetraamine, sulphuric acid, nitric acid, magnesium sulphate, xylenol orange, eriochrome black T, potassium peroxodisulphate, acetone and quinol, were of BDH grade.

Preparation of Chitosan

Chitin material from African giant snail shell (*Archachatina marginata*) 25.0 g of powder prepared by grinding dried snail shell (bought from local market in Benin City, Nigeria) was heated with 1.2 L 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 was treated with drop wise addition of 40% aqueous sodium hydroxide solution until a white flocculant's precipitate was formed at pH of 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 taken as pure chitosan because it 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% H₂SO₄ and in 0.5-10% acetic acid; it is insoluble in 0.5% and above 7.5% H₂SO₄.

Preparation of Metal Ion Solutions

Solutions of Pb²⁺, Cd²⁺ and Ni²⁺ were prepared at varying concentrations of 50, 100, 200, 400 and 500 mg L⁻¹ for each metal ion. The pH of all solutions was at near neutrality (6.5-7.5). Hundred milliliters portion of each solution was used for sorption experiments.

Grafting Method

Grafting copolymerization, which can be carried out on pre-existing polymers (natural or synthetic) has the advantage of incorporating properties such as elasticity, sorbency, ion-exchange capabilities, thermal resistance and resistance to microbial attacks onto a polymer (Matijevic and Stryker, 1966). Grafting modifies both physical and chemical properties of the polymer. The grafting procedures employed in this were based on the method described by Lepouner and Hui, (1975). The chitosan grafted with acrylamide is otherwise referred to as CGA in this research.

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 bound 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

Table 1 show that the optimum temperature for adsorption of metal ions unto 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 (Okuo and Ozioko, 2001; Okolo and Okuo, 2004).

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 these higher temperatures. The chitosan grafted with acrylamide, CGA, has a higher adsorption capacity than untreated chitosan. For example, in Table 1 the amount of Pb²⁺ ions ranged 43.88-56.19%. Compare this with that adsorbed onto CGA: 49.4-65.56%. Similarly, for Cd²⁺ ions, untreated chitosan gave 27.50-58.60%, while CGA yielded 56.49-97.90% (Table 1 and 2a, respectively).

The uptake levels of nickel ion at optimum temperature (45°C) by untreated chitosan and CGA differ from those observed for Pb²⁺ and Cd²⁺ ions. For instance, the amount of Ni²⁺ ions adsorbed using untreated chitosan and CGA ranged between 41.30-58.90 and 29.6-64.8%, respectively (Table 1 and 2). This might be due to variations in the characteristics of the adsorbate, whose hydration energy and ionic size are 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 (NH₂) 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.

Table 1: Effect of temperature on sorption of Ni²⁺, Pb²⁺ and Cd²⁺

Initial conc. (mg/100 mL)	Amount adsorbed (mg/100 mL)								
	30°C			45°C			60°C		
	Cd ²⁺	Ni ²⁺	Pb ²⁺	Cd ²⁺	Ni ²⁺	Pb ²⁺	Cd ²⁺	Ni ²⁺	Pb ²⁺
20	4.20	5.92	6.53	11.72	11.78	12.12	9.64	8.26	7.40
40	8.92	9.47	7.40	11.00	16.52	17.52	10.16	11.28	8.53
60		13.03			25.95			16.56	
80	30.28	25.99	19.30	38.80	35.38	42.91	13.68	28.34	35.04
120	53.68		52.56	66.12		66.05	30.88		58.18
160	68.84		70.08	87.48		86.94	44.00		83.57
200	84.00		92.40	112.96		112.38	70.00		107.83

Table 1: Continued

Initial conc. (mg/100 mL)	D = loga _s / logc _s								
	30°C			45°C			60°C		
	Cd ²⁺	Ni ²⁺	Pb ²⁺	Cd ²⁺	Ni ²⁺	Pb ²⁺	Cd ²⁺	Ni ²⁺	Pb ²⁺
20	0.52	0.68	0.72	1.18	0.1.18	1.20	0.96	0.86	0.79
40	0.64	0.66	0.58	0.71	0.89	0.92	0.69	0.74	0.62
60		0.66			0.92			2.26	
80	0.87	0.82	0.72	0.98	0.94	1.04	0.63	0.85	0.92
120	0.95		0.94	1.05		1.05	0.76		0.98
160	0.94		0.95	1.04		1.04	0.80		1.02
200	0.93		0.87	0.97		1.06	0.88		1.04

Table 1: Continued

Initial conc. (mg/100 mL)	Percentage retention (%)								
	30°C			45°C			60°C		
	Cd ²⁺	Ni ²⁺	Pb ²⁺	Cd ²⁺	Ni ²⁺	Pb ²⁺	Cd ²⁺	Ni ²⁺	Pb ²⁺
20	21.00	29.60	32.70	58.60	58.90	60.60	48.20	41.30	37.00
40	22.30	31.10	18.50	27.50	41.30	43.88	25.40	29.53	21.00
60		21.72			43.25			27.60	
80	44.73	32.49	24.13	48.50	44.23	53.36	17.10	35.43	43.80
120	44.73		43.80	55.10		55.04	25.73		48.48
160	43.03		43.80	54.68		54.34	27.50		52.23
200	42.00		46.20	56.48		56.19	35.00		53.92

Table 2a: Sorption of Pb²⁺ and Cd²⁺ ions by CGA at 45°C

Initial conc. (mg/100 mL)	Equilibrium conc (mg/100 mL)		Amount adsorbed (mg/100 mL)		D = log a _s / 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

Table 2b: Sorption of Ni²⁺ ion by CGA at 45°C

Initial conc. (mg/100 mL)	Equilibrium conc (mg/100 mL)	Amount adsorbed (mg/100 mL)	D = log a _s / 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

The distribution coefficient, D, of Pb²⁺ ion for chitosan and CGA ranged between 0.92-1.20 and 0.99-1.24, respectively. That of Cd²⁺ ion ranged from 0.71-1.18 and -3.39-1.20 for chitosan and CGA, respectively. Similarly, the values for Ni²⁺ 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, Cd²⁺ ions with distribution coefficient of -3.39 to 1.07 for the CGA would be more easily removed from waste waters containing Pb²⁺, Cd²⁺ and Ni²⁺ contaminants.

Figure 1-3 show the Freundlich isotherms for the adsorption of Cd²⁺, Pb²⁺ and Ni²⁺ ions, respectively on chitosan and CGA. The Freundlich isotherm equation is given as:

$$a = KC^{1/n}$$

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:

$$\log a = \log K + \frac{1}{n} \log C$$

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 estimation of K. Thus, the values of n and K were determined to be in the range of 0.5-0.63 mg/100 mL for chitosan and 1.08-1.16 mg/100 mL for CGA, with respect to Pb²⁺ ion. The

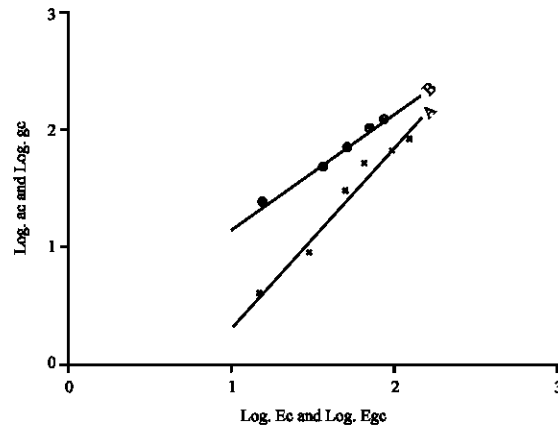


Fig. 1: Cd^{2+} ion uptake on chitosan and CGA. A = graph of $\log. ac$ vs. $\log. Ec$; B = graph of $\log. gc$ vs. $\log. Egc$. ac = amount of Cd^{2+} ion adsorbed per unit mass of chitosan; Ec = equilibrium conc. of Cd^{2+} ion after adsorption on chitosan; gc = amount of Cd^{2+} ion adsorbed per unit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

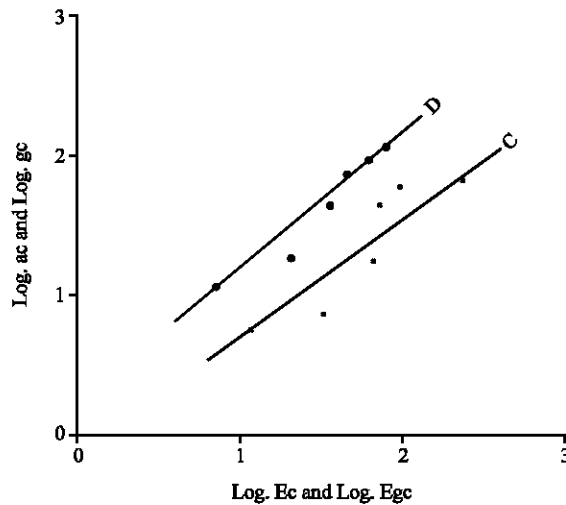


Fig. 2: Pb^{2+} ion uptake on chitosan and CGA. C = graph of $\log. ac$ vs. $\log. Ec$. D = graph of $\log. gc$ vs. $\log. Egc$. ac , Ec , gc , and Egc as in Fig. 1

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 mechanism 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.

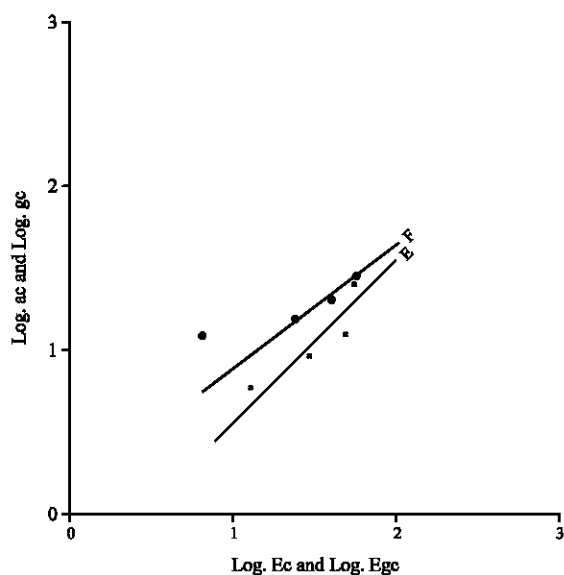


Fig. 3: Ni²⁺ ion uptake on chitosan and CGA. E = graph of log. ac vs. log. Ec; F = graph of log. gc vs. log. Egc. ac, Ec, gc and Egc as in Fig. 1

CONCLUSIONS

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 metal-laden wastewaters. In addition, this study also shows that apart from the nature of adsorbent, other factors such as metal ion concentration and temperature also play a significant role in metal ion uptake.

REFERENCES

- Chanda, M., L.F.O. Driscou and G. Rampel, 1983. Reactive Polymers. Longman, London, pp: 183- 281.
- Glasstone, S. and D. Lewis, 1983. Elements of Physical Chemistry, 2nd Edn., Macmillan Press Ltd., London, pp: 558-601.
- Jackson, A.R.W. and J.M. Jackson, 1996. Environmental Science, Longman, London. pp: 289- 336.
- Lee, J. D., 1999. Concise Inorganic Chemistry, 5th Edn., Blackwell Science Ltd. Osney Mead, Oxford, London, pp: 149-162.
- Lepoutre, S.H. and S.H. Hui, 1975. The mechanical and chemical properties of graft cellulosic materials. J. Applied Polym. Sci., 19: 1257-1262.
- Manahan, S.E., 1994. Environmental Chemistry, 6th Edn., Lewis Publishing, London, pp: 676-677.
- Matjevic, E. and L. Stryker, 1966. Physical and chemical properties of graft copolymerization. Discussions Faraday Soc., 42: 187-192.
- Miroslav, R. and N.B. Vladimir, 1999. Practical Environmental Analysis. The Royal Society of Chemistry, UK., 6: 7-267.

- Randall, J.M., V.G. Randall, G.M. McDonald, R.N. Young and M.S. Masri, 1979. Removal of trace quantities of nickel from solution. *J. Applied Polym. Sci.*, 23: 727-732.
- Ricordel, S., S. Taha, I. Cisse and G. Dorange, 2001. Heavy metals removal by adsorption onto peanut husk carbon: characterization, kinetic study and modeling. *Separation and Purification Technol.*, 24: 389-401.
- Okolo, P.O. and J.M. Okuo, 2004. Heavy metal ions adsorption by chemically treated coconut husk, shell and palm kernel fibre. *Intl. J. Chem.*, 14: 60, 185-195.
- Okuo, J.M. and A. Ozioko, 2001. Adsorption of lead and mercury ions on chemically treated periwinkle shells. *J. Chem. Soc. Nigeria*, 26: 60-65.
- Okuo, J.M., S.B. Sanni and S.U. Aigbedion, 2006. Selective biosorption of heavy metal ions from aqueous solution by pre-treated Nigerian fresh water algae. *Trends Applied Sci. Res.*, 1: 83-90
- Okuo, J.M. and P.O. Okolo, 2006. Removal of heavy metal ions by blended periwinkle shells. *J. Applied Sci. Scientific Res.*, 6: 567-571.
- Vogel, A.I., 1961. *A Textbook of Quantitative Inorganic Analysis*, 3rd Edn., Longman, London. pp: 415-456.