Indian J. Innovations Dev., Vol. 1, No. 1 (Jan 2012)

ISSN 2277 - 5390

Application of marine biomass for the removal of metals from industrial wastewater

Muhammad MN[1], Nwaedozie JM[2]

[1 &2] *Department of Chemistry, Nigerian Defence Academy, Kaduna, Nigeria*

Abstract

A batch adsorption experiment was carried out using marine algae-seaweed (Ascophyllum nodosum) as adsorbent for metal removal at two temperatures (23.5°C and 37°C) and four pH values (2, 5, 7 and 10). Atomic Absorption Spectroscopy (AAS) adsorption results show maximum adsorption capacities of 93.41% for lead at pH 2, 53.13% for cadmium at pH 10 and no adsorption for chromium throughout the pH range and temperature were found to have no significant effect on the adsorption process, especially for cadmium and lead. However, the effect of pH was significant and varied with each metal. These results were found to be comparable to results reported from previous works. The results show that the removal efficiency of each adsorbent is highly dependent on pH, and metal ion removal occurred in the preferential order lead > cadmium > chromium, depicting strong contributions from the ionic radius of each metal ion. These results demonstrate the immense potential of the adsorbent as alternatives for metal removal from industrial effluent treatment.

Keywords: Adsorbent; Adsorption; Trace metals; Sludge.

Introduction

Heavy metal contamination in industrial effluents has been an issue of environmental and public health concern since the advent of industrialisation, owing to their non-biodegradable, toxic and bio-accumulative nature (Bailey *et al*., 1999; Nomanbhay and Palanisamy, 2005). The rapid growth in global population and urbanisation has driven an exponential increase in industrial activities, which is accompanied by an increase in the amount of industrial wastes being discharged into the environment. Hence, the increase in heavy metals such as Cadmium, Mercury, Lead, Copper, Zinc, Nickel and Chromium posing significant risk to soil, water and human health. Heavy metals are discharged into the environment by industries such as mining, textile, petro-chemical, tannery and plating among others.

Various treatment methods have been employed in the removal of heavy metals from industrial effluents. Among them, include chemical precipitation, membrane filtration, ion exchange, reverse osmosis, electrodialysis, solvent extraction, evaporation, oxidation, activated carbon adsorption (Shukla *et al*., 2002; Papparlado *et al*., 2010). However, these methods are often expensive and difficult to maintain due to high capital and operational costs, as well as, extra cost of treating the resultant sludge generated before disposal. The generated secondary waste, apart from requiring additional treatment along with the accompanying cost, also poses disposal hazards and pollution risks to the environment (Kumar, 2006). Hence, the need for cost-effective and efficient naturally abundant alternatives to the conventional methods of metal contaminated industrial wastewater treatment (Oilgae, 2010).

In response to this need, studies on cheaper methods of treating metal-enriched industrial wastewater involving the possible use of low-cost and commonly available organic materials with high adsorptive capacities is now a growing research area (Oboh, Aluyor and Audu, 2009). Low–cost organic materials which have been found to possess potentials for viable use in the treatment of industrial wastewater include reed plant, tree bark, moss, cotton wool, reed plant, corn hobs, rice husk, orange peel, banana peel, sawdust, apple-waste, mango peel, etc. (Bailey *et al*., 1999; Kanamadi, Ahalya and Ramachandra, 2006). The choice of an organic adsorbent usually depends on a number of factors, which include availability, location, locality, seasonality, cost-effectiveness, etc.

Apart from availability, location, seasonality and cost-effectiveness, studies have demonstrated that the use of low-cost adsorbents has distinct advantages over conventional methods of metal removal from industrial wastewater (Gardea-Torresdey *et al*., 2004). This property has fuelled the growing attraction for researchers towards the use of readily available organic adsorbents for the removal of heavy metals from wastewater. These advantages include: low cost, high efficiency, reduced production of sludge, ease of regeneration of biosorbents and metal recovery (Sud, Mahajan and Kaur, 2008). Other sustainable benefits to industries include; meeting statutory discharge limits for industrial wastewater and enhancement of their corporate social and environmental responsibility profiles (Shukla *et al*., 2002). This paper is aims to assess the effectiveness of a commonly available marine biomass for the treatment of industrial effluents. The paper also investigated the effects of temperature and pH on the adsorptive capacities of the selected bio-resource. The choice of this material was based on its availability in large quantity and low cost. It is found abundantly along coastline and beaches in both tropical and temperate region on the world, which constitutes a nuisance to coastal vessels and fishermen.

Materials and Methods

Preparation of Adsorbents

The marine biomass used as biosorbent for this study was seaweed (*Ascophyllum nodosum).* It *was* used in its natural forms after washing and drying and devoid of any chemical pre-treatment. It was collected at the Broughty Ferry beach, Dundee, Scotland. After collection, it was washed with tap water, followed by distilled water to remove the sand and stones entangled in them. It was then dried in the oven at 105°C for 24 hours. After which the sample was blended into a powder using a commercial blender and further reduced to finer particles of 0.5mm particle-size using Fritsch Rotor Speed Mill-Pulverisette 14 and stored in clearly-labeled transparent containers.

Metal Solutions

All metal salts and chemical reagents used were of analytical grade (Aldrich U.K). Standard Stock solutions of Cd^{2+}, Pb^{2+}, and Cr^{3+} were prepared to the required concentrations in mg/L by dissolving the appropriate amount of Cadmium solid, KCrO4, and $Pb(NO_3)_2$ in de-ionized water. De-ionized water was used for the preparation of standard solutions.

Instrument and Apparatus

A pre- and post adsorption determination of the types and distribution of functional groups present in the dry adsorbent samples was carried out by Perkin Elmer Fourier Transform Infrared (FTIR) RX1 spectroscopy, using Potassium Bromate (KBr) disc to prepare the feedstock. The spectral range varied from 4000 to 400cm^{-1}. The Cd^{2+}, Pb^{2+}, and Cr^{3+}, concentrations were determined by using Perkin-Elmer Model Atomic Absorption Spectrometer (AAS) equipped with deuterium lamp background correction. All pH measurements were taken with a Hanna Educational HI 208 ion-meter and calibrated with buffer solutions of pH 4.0, 7.0 and 10.0.

Adsorption Experiment

The adsorption experiments were carried out in Batch mode at various pH (2, 5, 7 and 10), temperature (23.5°C and 37°C) and adsorbent dose of 20gl^{-1}.for a contact time of 180min. For each 50ml of metal (Cd^{2+}, Pb^{2+}, Cr^{3+}) solution of 200mg/l was used and pH adjusted before adding adsorbent. The mixture was agitated on mechanical shaker for 180 min. After that, the mixture was centrifuged for 20 minutes at a speed of 5400 rpm using an Impact-5 Centrifuge to separate the supernatants from the adsorbent. The residual concentration of metals in the supernatant was determined using AAS. All the experiments were done in replicated and results averaged. The percentage removal and metal uptake efficiencies of all adsorbents were determined with following expressions:

$$\text{Metal uptake} = \frac{(C_i - C_f)}{C_i} \times 100 \qquad (1)$$

The amount of metal adsorbed, Q (mg metal/gram sorbent) was computed using equation 2.

$$Q = \frac{(C_i - C_f)\,V}{m} \qquad (2)$$

Where,
Q = Amount of metal adsorbed (mg/g)
C_i= Initial metal concentration in solution (mg/l)
C_f = Final metal concentration in supernatant after adsorption (mg/l)
V = Volume of solution (ml)
m = Mass of the adsorbent (g), which in this experiment = 1g, approximately.

Results and Discussions

Seaweed has been reported to be rich in other extracellular polymers on its cell wall matrix, with the alginate polysaccharide being responsible for ion-exchange capacity of the brown algae due to high concentration of carboxyl groups (Mehta and Gaur, 2005; Freitas, Delerue-Matos and Boaventura, 2009). The functional groups found to occur on the binding surface of seaweed include the carboxyl, hydroxyl, amine, phosphate and sulphate groups, as well as other chemical functional groups contained in cell sugars and proteins. However, the carboxyl and sulphate groups are thought to be the most active groups in the binding of metals during adsorption (Romera *et al*., 2007). The functionalities of these groups in adsorption have been reported to be pH-dependent.

Fourier Transform Infrared Analysis of Adsorbents

The FTIR spectral of adsorbent (seaweed) before and after adsorption of metals were used to determine the vibration frequency changes in the functional groups. The spectra of adsorbents were measured within the range of 400 – 4000cm^{-1} wave number. The pre-adsorption FTIR analysis results (fig.1d) suggested the presence of such functional groups as the carboxylic acid or alcoholic O-H bond stretching which may overlap with amine (N-H) bond stretching at peaks between 3250-3400 cm^{-1}; possible C=O bond of carbonyl or amide groups within 1640-1670 cm^{-1}; C-O and O-H bond stretching of alcohol and ethers at 1000-1260 cm^{-1} of the finger-print region. The post-adsorption FTIR results (figure 1e–1g) showed only slight changes suggesting no significant changes in distribution of the identified functional groups and probable uniformity in manner of adsorption as the adsorbent is organic and may bind metals in similar manners.

A deeper trough was observed at 1400 cm^{-1} suggesting possible binding of cadmium at this site. No significant change was observed after chromium adsorption which may explain the poor adsorption of chromium, possibly due to the effect of the high initial chromium content of seaweed. Lead adsorption showed a strikingly deeper trough at 1384.5 cm^{-1} indicating possible binding to the nitro N=O stretching. These identified regions may be indicative of functional groups responsible for the individual metal-binding activity of the adsorbent, apart from the groups indicated in previous studies (Kanamadi, Ahalya and Ramachandra, 2006).

Effect of Temperature and pH on the Adsorption of Metal Ions

The adsorption experiments were carried out at two temperatures, 23.5°C and 37°C; and four different pH values- 2, 5, 7 and 10 respectively. The effect of temperature and pH on the adsorption of each metal ion by the seaweed is shown in Figures 1a-1c. From the graphs, it can be seen that temperature had no significant effect on the percentage adsorption of metal ions by the adsorbent as similar percentage adsorptions are recorded at both temperatures for all the metals.

Cadmium adsorption at 23.5°C and 37°C yielded similar percentage adsorptions at all pH values except for pH 7 where adsorption at 37°C

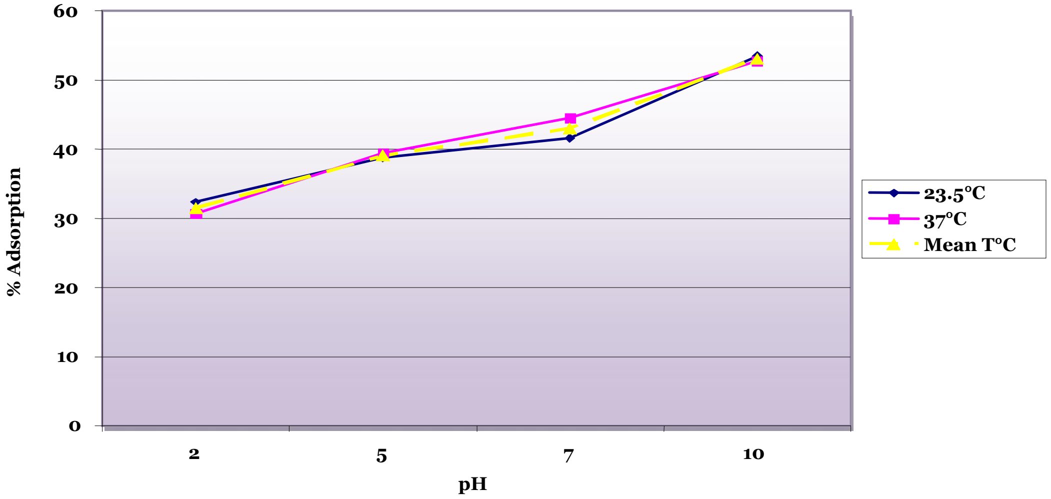

Fig. 1a. Effect of temperature and pH on cadmium adsorption using seaweed.

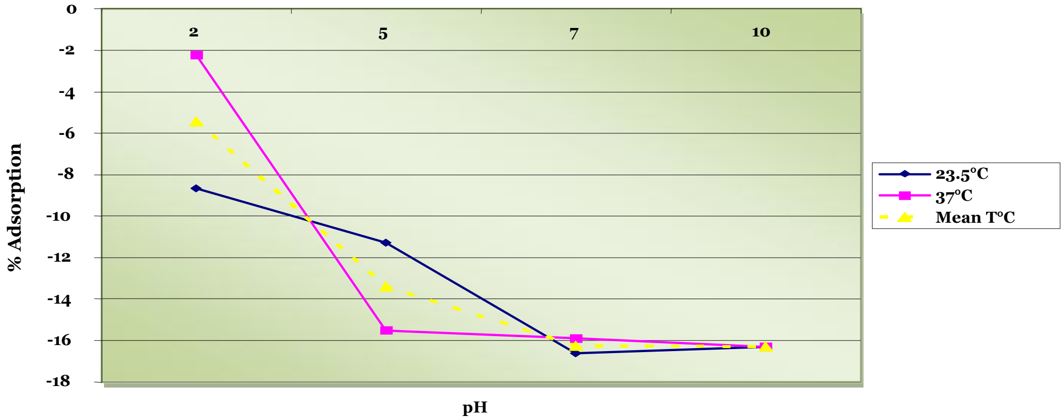

Fig. 1b. Effect of temperature and pH on chromium adsorption using seaweed.

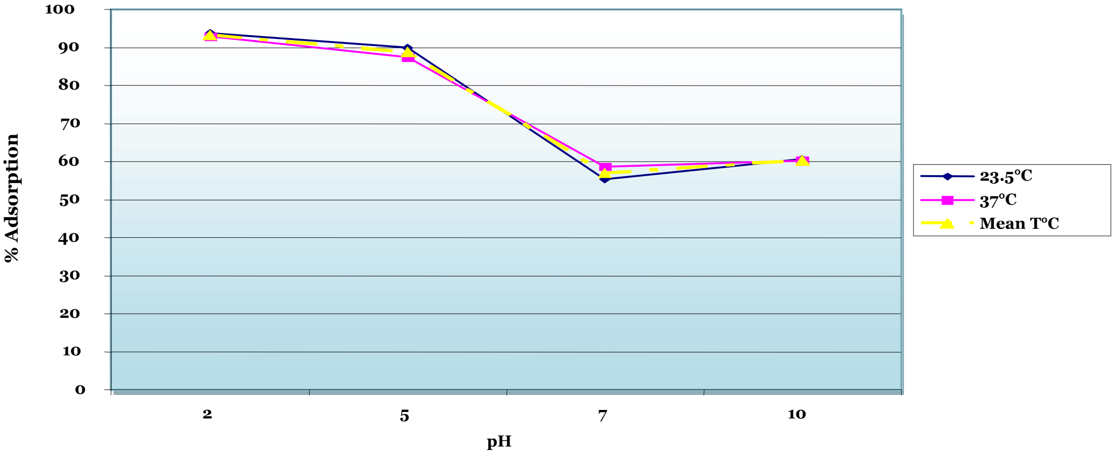

Fig. 1c. Effect of temperature and pH on lead adsorption using seaweed.

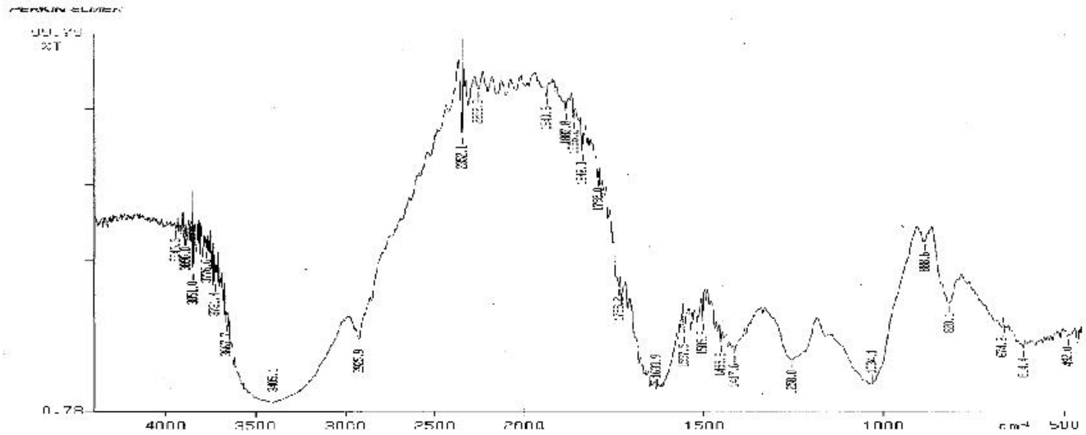

Fig. 1d. FTIR spectrum of seaweed (Pre-adsorption).

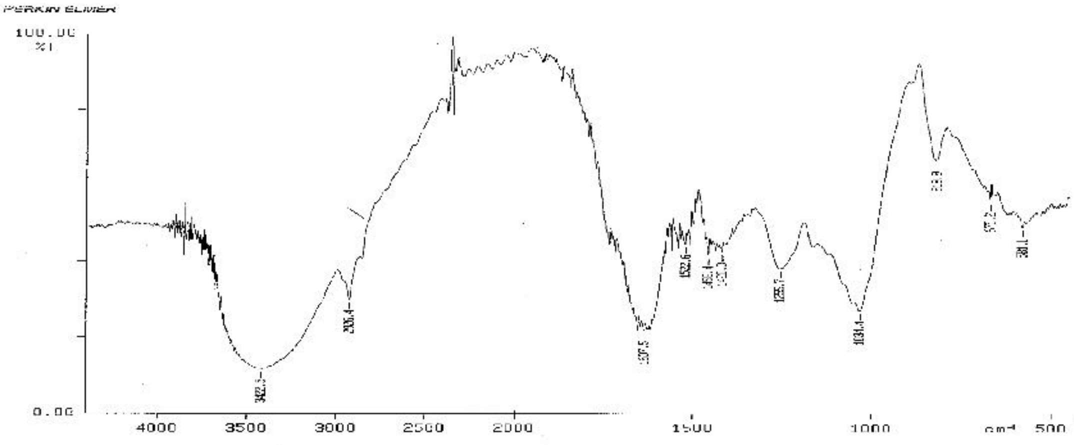

Fig. 1e. FTIR spectrum of seaweed after chromium adsorption

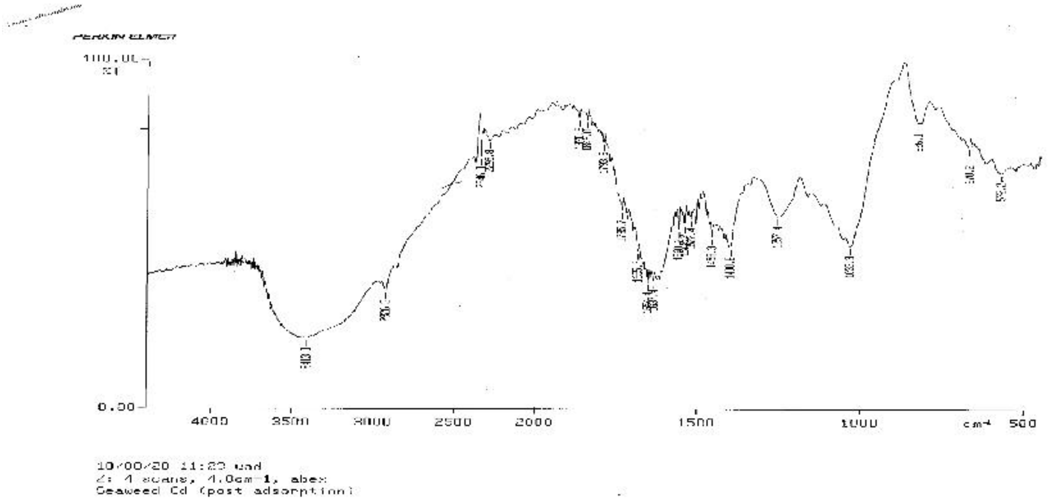

Fig. 1f. FTIR spectrum of seaweed after cadmium adsorption.

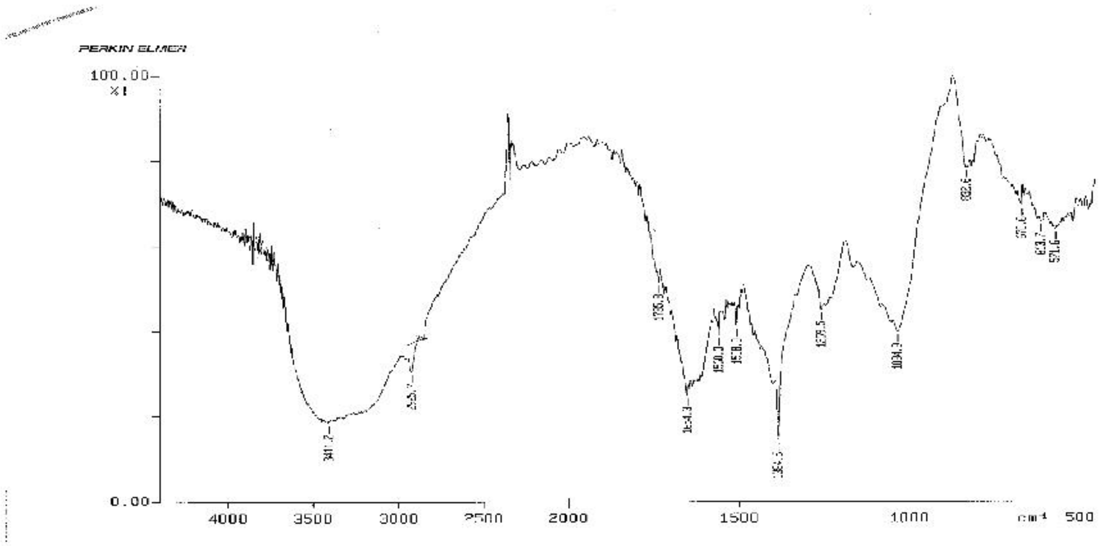

Fig. 1g. FTIR spectrum of seaweed after lead adsorption

(44.55%) can be seen to be higher than that at 23.5°C (41.60%), (Fig.1a). The percentage adsorption of cadmium can also be seen to increase gradually with increase in pH with the least adsorption of 31.53% occurring at pH 2 and the highest of 53.13% at pH 10. Adsorption at pH 5 and 7 were 39.10% and 43.08%, respectively. This trend suggests an enhanced capacity for cadmium uptake in alkaline solutions. Hence, the poor adsorption of cadmium onto the adsorbent surface at acidic pH may depend on ionic attractions as the ligands on the adsorbent surface are positively-charged due to close association with hydronium ions (H_3O^+) or H^+, causing reduced attraction for the cadmium cations and as such, a reduced rate of adsorption (Yu *et al.*, 2001; Ho, 2005). However, as pH increases, more negatively-charged ligands such as the carboxyl or amino groups are progressively exposed as a result of proton release. This increases the negative charge density on the seaweed surface, thereby attracting the cadmium cations onto the adsorbent binding sites until equilibrium is attained and adsorption begins to decline due to possible precipitation of insoluble hydroxides of the metal ions which has been reported at alkaline pH values (Goyal *et al.*, 2008; Hussain, Salleh and Milow, 2009). This precipitation may be responsible for the 53.13% cadmium removal at pH 10 by seaweed observed in this study.

Percentage chromium adsorption generally decreased with increasing pH with its highest adsorption at pH 2 (Fig. 1b). This may be attributed to the form in which chromium ion exists at such acidic pH which facilitates its removal from acidic solution than from alkaline solution, as well as, the dominating charge on the adsorbent surface at such pH (Bansal *et al.*, 2009). Chromium exists only in two oxidation states in nature +3 and +6 and when in solution, the Cr(III) state hydrolyses in a complicated manner to produce Cr(VI). At acidic pH, the predominant species of Chromium are $Cr_2O_7^{-2}$, $HCrO_4^{-1}$, H_2CrO_4, $Cr_3O_{10}^{-2}$ and $Cr_4O_{13}^{-2}$. Thus, at pH 2, Cr(VI) exists mainly in the anionic form, $HCrO_4^{-1}$, and its adsorption may be favoured by highly protonated or positively-charged adsorbent surface. However, this level of protonation of the adsorbent surface reduces as pH increases, thus, slowing down the rate of adsorption. A further increase in pH leads to a situation where the abundant OH^- groups of the adsorbent polysaccharides start to compete with the $HCrO_4^{-1}$ ions for the available protonated binding sites, leading to OH^- groups being preferentially adsorbed due to their predominance over the chromate ion in solution. This reduce action of chromium adsorption as supprted by similar studies (Davies, Volesky and Mucci, 2003**;** Olayinka, Alo and Adu, 2007). Other results of higher adsorption of chromium at low pH values have been reported in earlier studies (Kanamadi, Ahalya and Ramachandra, 2006; Bhattacharya, Mandal and Das, 2006; Olayinka, Alo and Adu, 2007; Dhungana and Yadav, 2008/2009; Olayinka, Oyedeji and Oyeyiola, 2009 and Bansal *et al*., 2009). Considering the pre-adsorption chromium content per adsorbent gram, it is possible that the already bound chromium ions may have competitively impeded the uptake of the chromium ions in solution by occupying some of the adsorbent binding sites, thereby contributing to the poor percentage adsorption of chromium by the seaweed which had some concentration of chromium prior to the adsorption experiments. Maximum adsorption at such acidic pH may have practical implications because discharging treated wastewater at such acidic pH may entail a lot of health and safety issues and chemical requirements. This is because such acidic wastewater would need to be neutralized before being discharged into the environment, unless the receiving water body is already highly alkaline due to prior pollution. In which case, such acidic discharge would help restore the neutrality of the aquatic environment. Otherwise, such discharge into a neutral aquatic environment may increase the acidity of the water thereby causing precipitated metals to go back into solution. This may increase the level of toxicity due to dissolved metals and may cause loss of aquatic life-forms.

The percentage lead adsorption decreased with increasing pH until pH 7 before increasing slightly at pH 10 (Fig.1c). Maximum adsorption of 93.41% occurred at pH 2 and the least of 57.04% at pH 7, with the difference in percentage adsorption highest between the 88.77% and 57.04% recorded at pH 5 and 7, respectively. The high removal of lead at pH 2 than at higher pH may be indicative of an enhanced ability to absorb lead from solution in acidic solution than in basic solutions, although this observation is considered unusual as most studies have reported an increase in the uptake of lead from solution with increasing pH until equilibrium is attained around pH 5 before a decline in adsorption starts to occur (Souag *et al*., 2009; Hussain, Salleh and Milow, 2009). This unexpected result suggests that electrostatic interactions alone may not suffice in explaining the changes in lead uptake with variations in pH, as there could be other or multiple mechanisms at play in the removal of lead from solution at such very acidic pH (Jin and Bai, 2002). Which one is similar to lead adsorption using chitosan/PVA (poly vinyl alcohol) that a decrease in solution pH resulted in increase in lead uptake from solution (Jin and Bai, 2002), pH 5 yielded the highest percentage lead removal of 88.8% in this study and this approximates the degree of lead removal reported in most previous works at this pH (Ho, 2005; Souag *et al*, 2009; Hussain, Salleh and Milow, 2009).

Conclusion

The results from this study indicate that the studied seaweed (*Ascophyllum nodomus*) is suitable for use in the removal of metal ions from industrial effluents. Adsorptive capacity and metal removal efficiency of the adsorbent studied varied significantly with each metal ion and with pH but not with temperature. Adsorption of cadmium increased with increase in pH while that of chromium exhibited an inverse relationship with increase in pH. The trend of lead adsorption varied with increasing pH. The efficiency of adsorbent per metal ion presented interesting results comparable to results from previous works. Chromium adsorption was generally poor exhibiting no efficiency for chromium removal but yielded maximum lead and cadmium removal of 93.41% and 53.13% at pH 2 and 10 respectively. The results show that the removal efficiency of each adsorbent is highly dependent on pH, and Metal ion removal occurred in the preferential order lead >cadmium>chromium, depicting strong contributions from the ionic radius of each metal ion. Based on this trend, seaweed is considered an efficient adsorbent for cadmium in neutral or alkaline solutions and for lead in acidic solutions.

References

1. Bailey SE, Olin TJ, Bricka RM and Adrain DD. (1999). A Review of Potentially Low-cost Sorbents for Heavy Metals. *Water Resources*. 33(11), 2469-2479.
2. Bansal M, Grag U, Singh D and Garg VK. (2009). Removal of Cr(VI) from Aqueous Solutions using Pre-Consumer Processing Agricultural Waste: A Case Study of Rice Husk. *Journal of Hazardous Materials*. 162(1), 312-320.
3. Bhattacharya AK, Mandal SN and Das SK. (2006). Removal of Cr (VI) From Aqueous Solutions by Adsorption onto Low-Cost Non-Conventional Adsorbents. *Indian Journal of Chemical Technology*. 13, 576-583.
4. Davies TA, Volesky B and Mucci A. (2003). A Review of the Biochemistry of Heavy Metal Biosorption by Brown Algae. *Water Resources*. 37, 4311-4330.
5. Dhungana TP and Yadav PN. (2008/2009). Determination of Chromium in Tannery Effluent and Study of Adsorption of Cr(VI) on Sawdust and Charcoal from Sugarcane Bagasses. *Journal of Nepal Chemical Society*. 23.
6. Freitas O, Boaventura R and Delerue-Matos C. (2006). Adsorption Study of Lead By *Ascophyllum nodosum* using a Factorial Experimental Design. *Combined and Hybrid Adsorbents*. 269-274.
7. Freitas O, Delerue-Matos C and Boaventura R. (2009). Optimization of Cu(II) Biosorption onto *Ascophyllum nodosum* by Factorial Design Methodology. *Journal of Hazardous Materials*. 167(1-3), 449-454.
8. Gardea-Torresdey JL, De-la-Rosa G and Peralta-Videa JR. (2004). Use of Phytofiltration Technologies in the Removal of Heavy Metals: A Review. *Pure and Applied Chemistry*. 76(4), 801-813.
9. Hussein H, Ibrahim SF, Kandeel K and Moawad H. (2004). Biosorption of Heavy Metals from Waste Water using *Pseudomonas* sp. *Environmental Biotechnology*. 7(1).
10. Hussain MA, Salleh A and Milow P. (2009). Characterisation of the Adsorption of Lead(II) by the Non-living Biomass *Spirogyra neglecta* (Hasall) Kutzing. *American Journal of Biochemistry and Biotechnology*. 5(2), 75-83.
11. Jin L and Bai R. (2002). Mechanism of Lead Adsorption on Chitosan/PVA Hydrogel Beads. *Langmuir*. 18: 9765-9770.
12. Kanamadi RD, Ahalya N and Ramachandra TV. (2006). Biosorption of Heavy Metals by Low-Cost Adsorbents. CES Technical Report-112. *Energy and Wetlands Research Group*.
13. Karanam Srinivasa Rao, Shashi Anand, and Paladugu Venkateswarlu. (2010). Adsorption of cadmium (ii) ions from aqueous solution by tectona grandis L.F. (Teak leaves powder). *Bio-resources*, 5(1), 438-454.
14. Kumar U. (2006). Agricultural Products and By-products As a Low-cost Adsorbent for Heavy Metal Removal from Water and Wastewater: A Review. *Scientific Research and Essay*. 1(2), 033-037.
15. Mehta SK and Gaur JP. (2005). Use of Algae for Removing Heavy Metal Ions from Wastewater: Progress and Prospects. *Critical Reviews in Biotechnology*. 25, 113-152.
16. Nomanbhay SM and Palanisamy K. (2005). Removal of Heavy Metal from Industrial Wastewater Using Chitosan-coated Oil Palm Charcoal. *Electronic Journal of Biotechnology,* ISSN: 0717-3458. 8(1).
17. Oboh I, Aluyor E, and Audu T. (2009). Biosorption of heavy meatl ions from Aqueous Solutions Using a Biomaterial. *Leonardo Journal of Sciences*. 14, 58-65.
18. Oilgae (2010). *New Technologies in Heavy Metals Removal from Wastewater*. [Online]. Available from: http://www.oilgae.com/algae/cult/sew/new/hmr/hmr.html [Accessed 21 May 2010].
19. Olayinka KO, Alo BI and Adu T. (2007). Sorption of Heavy Metals from Electroplating Effluents by Low-Cost Adsorbents II: Use of Waste Tea, Coconut Shell and Coconut Husk. *Journal of Applied Sciences*. 7(16), 2307-2313.
20. Olayinka OK, Oyedeji OA and Oyeyiola OA. (2009). Removal of Chromium and Nickel Ions from Aqueous Solution by Adsorption on Mordified Coconut Husk. *African Journal of Environmental Science and Technology*. 3(10), 286-293.
21. Pappalardo L, Jumean F and Abdo N. (2010). Removal of Cadmium, Copper, Lead and Nickel from aqueous Solution by White, Yellow and Red United Arab Emirates Sand. *American Journal of Environmental Sciences*. 6(1), 41-44.
22. Romera E, Gonzalez F, Ballester A, Blazquez ML and Munoz JA. (2006). Biosorption with Algae: A Statistical Review. *Critical Reviews in Biotechnology*. 26, 223-235.

23. Romera E, Gonzalez F, Ballester A, Blazquez ML and Munoz JA. (2007). Comparative Study of Biosorption of Heavy Metals using Different Types of Algae. *Bioresource Technology*, 98, 3344-3353.
24. Shukla A, Zhang Y, Dubey C, Margrave JL and Shukla S. (2002). The Role of Sawdust in the Removal of Unwanted Materials from Water. *Journal of Hazardous Materials,* B95, 137-152.
25. Souag R, Touaibia D, Benayada B and Boucenna A. (2009). Adsorption of Heavy Metals (Cd, Zn and Pb) from Water Using Keratin Powder prepared from Algerien Sheep Hoofs. *European Journal of Scientific Research*. 35(3), 416-425.
26. Sud D, Mahajan G and Kaur MP. (2008). Agricultural Waste Material as Potential Adsorbent for Sequestering Heavy Metal Ions from Aqueous Solutions - A Review. *Bioresource Technology,* 99(14), 6017-6027.
27. Yu B, Zhang Y, Shukla A, Shukla SS and Dorris KL. (2001). The Removal of Heavy Metals from Aqueous Solutions by Sawdust Adsorption - Removal of Lead and Comparison of Its Adsorption with Copper. *Journal of Hazardous Materials,* 84(1), 83-94.