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A Comparative Study of Seven Materials as Sorbents for Removal of Metal Ions from Real Storm Water Runoff

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Among the various non-point sources, storm water runoff from urban areas has been recognized as a major contributor to a variety of water pollution problems in adjacent receiving bodies of water. Urban storm water runoff contains pollutants such as heavy metals, polycyclic aromatic hydrocarbons, and mineral oil hydrocarbons which are generally regarded as hazardous to water. In particular, the presence of heavy metals in runoff is of great concern due to their non-biodegradability. Sorption-based technology has been recognized to be a promising remediation method for removal of metal ions from aqueous streams. The present work examined the efficiency of seven low-cost materials (crab shell, *Sargassum* sp., Amberlite, chitosan, sawdust, peat and bagasse) as sorbents for metal removal from urban storm water runoff. The urban storm water runoff used in the study contained a range of metal ions (Cu, Ni, Co, Pb, Cd, Fe, Zn, Ca, Mg, Al, Na and K). The comparative evaluation indicated that both crab shell and *Sargassum* sp. performed exceedingly well in the removal of metal ions compared to other sorbents examined. SEM-EDX analysis of sorbents prior to and after sorption experiments was performed to provide mechanistic insights into the removal of metal ions from the storm water. Kinetic studies revealed that the sorption of metal ions by both crab shell and *Sargassum* sp. was very fast, which implies that these materials could be used in continuous storm water treatment processes. According to desorption experiments conducted in the study, it is possible to recover industrially-relevant metals such as Cu, Ni, and Zn and reuse the sorbents for next cycle of sorption.

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1. Introduction

The stormwater runoff from urbanized lands has the potential to change the health of water bodies, impact on aquatic habitats, recreation and aesthetics, or cause algae to grow uncontrollably (NSW-EPA, 1998). Among the contaminants, metal ions are a serious concern because of their tendency to bio-accumulate. These metals are either dissolved in the storm water, or are bound to particulates (Sansalone and Buchberger, 1997). However, their presence is strongly site-specific. Studies done in Ashdod, Israel, (Asaf et al., 2004) showed that the trace metal concentrations in storm water runoff were in the following ranges: manganese (0.001 - 0.516 mg/l), zinc (0.008 - 0.720 mg/l), copper (0.001 -0.079 mg/l), and lead (0.003-0.010 mg/l). In another characterization study, Walker et al. (1999) summarized the concentrations of heavy metals in urban runoff in the following concentration ranges: zinc (0.0007-22.0 mg/l), copper (0.00006 – 1.41 mg/l), and lead (0.00057-26.0 mg/l).

To reduce the metal concentrations in storm water to acceptable limits, simple and cost-effective treatment techniques are necessary. In recent years, several waste materials of biological origin have been identified to bind and remove metal ions from wastewater. The results of metal removal by these biosorbents are almost comparable to some of the well established adsorbents or ion-exchange resins (Vijayaraghavan and Yun, 2008). This study examined seven sorbents for their potential to treat simulated urban runoff comprises of different metal ions.

2. Materials and methods

Seven sorbents were used in the present study, which includes Amberlite (Amberlite XAD7, Sigma), chitosan (from crab shells, Practical grade, Aldrich), sawdust, peat, bagasse, crab shell and *Sargassum* sp. Peat (150 µm sieve size) was collected from was collected from Sungai Sembilan peat deposit, a sub province, 200 km away from city of Dumai in Sumatra, Indonesia. On the other hand, sawdust (0.5 – 1 mm) and bagasse (0.5 – 1 mm) were collected locally. Waste shells of *Portunus sanguinolentus* were collected from the local markets in Singapore and were washed, sun dried and crushed to a particle size in the range of 0.5 - 1 mm. The shell particles were then treated with 0.1 M HCl for 4 h followed by washing several times with deionized water and then dried in an oven at 60^0C overnight. Fresh biomass of *Sargassum* sp. was collected from the beaches of Labrador Park in Singapore. The biomass was extensively washed with deionized water and sun-dried. The dried biomass was then grounded to a particle size in the range of 0.5 - 1 mm.

Storm water runoff was simulated by adding different metals at different concentrations in real rain water. The simulated storm water runoff comprise of the following metals in milligrams per liter: 21.2 (Al), 20.2 (Fe), 9.4 (Na), 51.2 (K), 41.2 (Ca), 51.7 (Mg), 5.0 (Co), 4.5 (Ni), 5.1 (Cu), 4.4 (Zn), 1.0 (Pb) and 3.2 (Cd).

Experiments were conducted by bringing 0.2 g of sorbent into contact with 100 ml of storm water runoff in a 250 mL Erlenmeyer flasks kept on a rotary shaker at 160 rpm and 23 ± 2^0C. After 3 h, the reaction mixture was filtered through a 0.45 µm PTFE membrane filter. Each filtrate was acidified and analyzed for aqueous metal content by ICP-AES. To determine the major mechanism responsible for biosorption, the metal-loaded biosorbents were dried, coated with thin layer of platinum and analyzed by scanning electron microscopy (SEM) equipped with energy dispersive X-ray analysis (JEOL, JSM-5600 LV).

3. Results and discussion

3.1 Screening

First experiments were conducted with seven different sorbents for metal removal from storm water runoff. Table 1 shows the performance of different sorbents on metal removal. From various results reported in literature on urban storm water runoff (Asaf et al., 2004; Walker et al., 1999), the collected rainwater was simulated with thirteen metal ions. Among the sorbents tested, both crab shell and *Sargassum* were able to biosorb most of the metal ions. The remaining sorbents were able to sorb only limited number of metal ions. The commercial ion-exchange resin, Amberlite XAD7, was not able to sorb any of metal ions examined. In the case of chitosan, it performed well for some metal ions such as Fe, Al, Cu and Pb. However, it showed very little potential to decrease the concentrations of light metal ions. Other low-cost sorbents such as bagasse, peat and sawdust showed only modest adsorption capacity towards most of the metal ions. Conversely, the marine algae *Sargassum* performed reasonably well in biosorption of heavy metal ions; especially it exhibited more than 90% removal towards Cu, Pb and Al. While the seafood industry waste, crab shell, performed very well in heavy metal biosorption, with more than 94% removal efficiency was observed towards all heavy metal ions. However, it is worth noting that the concentrations of most of the light metal ions in the final effluent were greater than the inlet storm water runoff. This was not only in the case of crab shell, but for most of the examined sorbents. This is because most of the sorbents were previously loaded or comprises light metal ions, which when contacted with runoff release the ions into the solution. For instance, the marine algae acquires Na, K, Ca and Mg from seawater, which when contacted with metal solution exchange these light metal ions with heavy metal ions from solution due to ion-exchange mechanism. From the experimental results, both *Sargassum* and crab shell were selected for further studies.

Table 1. Performance of different sorbents on urban storm water runoff (in mg/l).

Metals	Control	Amberlite	Chitosan	Sargassum	Crab shell	Bagasse	Saw dust	Peat
Al	21.2	17.5	0.13	1.83	1.08	20.9	21.7	11.6
Na	52.4	70.2	51.6	68.9	52.1	53.9	52.1	51.7
K	51.2	51.1	50.8	64.9	54.6	52.1	50.9	51.7
Ca	48.2	48.3	49.4	74.5	164	48.8	51.3	49.5
Mg	51.7	50.2	50.4	66.5	79.3	51.8	69.4	72.8
Co	4.96	4.88	4.89	3.56	0.31	4.91	4.89	4.98
Ni	4.85	4.87	4.05	2.71	0.24	4.86	4.84	4.81
Cu	5.14	5.04	0	0.45	0.28	5	4.54	1.14
Zn	4.39	4.39	3.71	2.67	0.04	4.34	4.73	4.5
Pb	1.01	0.80	0	0	0	0.50	0	0
Cd	3.22	3.29	2.07	1.02	0.01	3.19	3.2	3.12
Fe	20.8	19.6	0.15	7.55	0.09	20.1	21.1	15.8

3.2 SEM examination

The scanning electron microscopy (SEM) equipped with EDX was used to analyze the components and morphology of biosorbent surface. Surface protuberance and microstructures can be observed in Figure 1, which may be due to calcium and other salt crystalloids. Crab shell comprises mainly calcium carbonate and chitin along with some proteins. Also through EDX analysis (Figure not shown), strong Ca peaks were observed. The peaks corresponding to carbon, nitrogen, oxygen, sulfur, and phosphorous were recorded in the EDX spectrum. These elements are present in the crab shell as the main constituents of chitin and protein. After biosorption, considerable changes in surface morphology of crab shell were apparent. Surface protuberances decreased and thin layer of deposition was observed (Figure 1). Through EDX analysis (Figure 3), peaks of all the metal ions examined were observed in the sample along with all other components identified in control crab shell sample. The main mechanism responsible for crab shell biosorption is micro-precipitation. Specifically, calcium carbonate in crab shell favors micro-precipitation of metal ions as $CaCO_3$ dissociates to Ca^{2+} and CO_3^{2-}. Most of the metal ions readily form metal carbonates at mild acidic conditions. The precipitates were then adsorbed to the acetamido groups of chitin on the surface of crab shell. Thus, CO_3^{2-} and $–NHCOCH_3$ play a vital role in removal of metal ions.

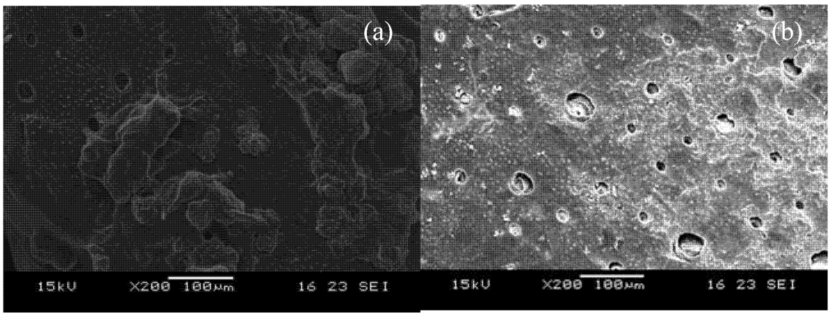

Figure 1. SEM images of crab shell before (a) and after (b) biosorption

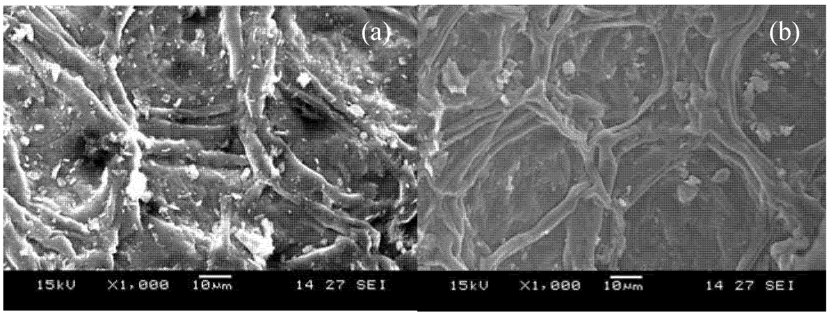

Figure 2. SEM images of Sargassum before (a) and after (b) biosorption

Figure 2 shows the SEM images of raw and metal-loaded *Sargassum* biomass. Surface protuberances and microstructures were observed, which may be due to calcium and other salt crystalloid deposition. After biosorption, protuberances become less obvious and the surface becomes flattened. The change in surface morphology is due to replacement of alkali and alkaline earth metals by metal ions in urban runoff. The EDX spectra (Figure 3) confirm the presence of all metal ions on the surface of *Sargassum*.

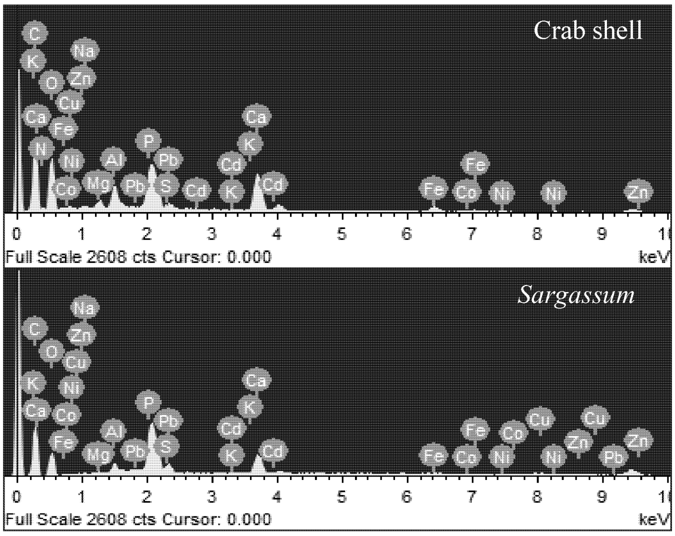

Figure 3. EDX spectra of crab shell and Sargassum after biosorption

3.3 Kinetics

Shown in Figure 4 are kinetics of metal biosorption onto crab shell and *Sargassum* biomass.

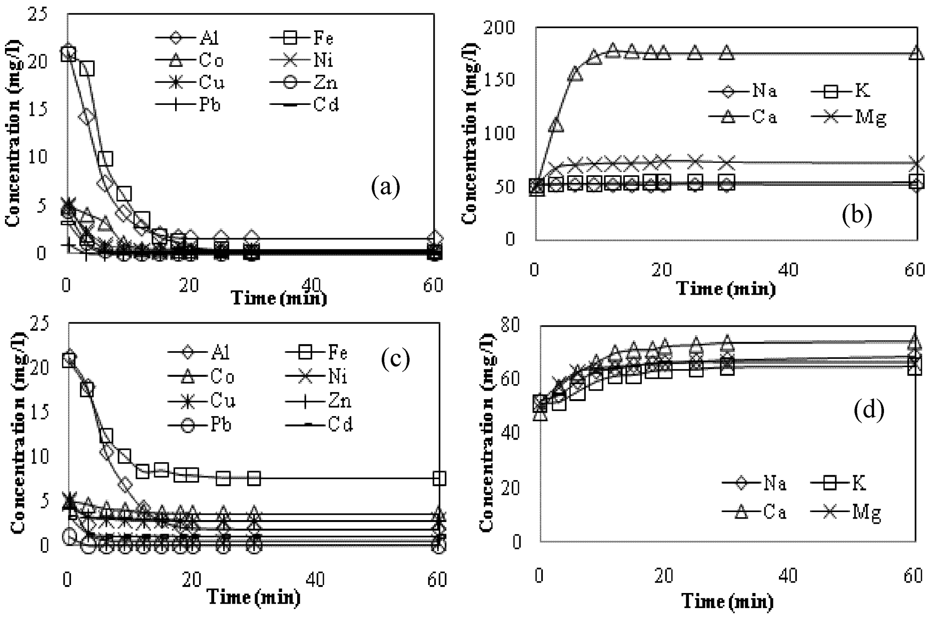

Figure 4. Kinetics of biosorption onto crab shell (a and b) and Sargassum (c and d).

The results obtained in kinetic experiments are in agreement with our findings that dissociation of $CaCO_3$ from crab shell and release of light metal ions from *Sargassum* biomass are responsible for heavy metal ions uptake. The increase in Ca concentration as the time progresses reveals that metal carbonate micro-precipitation plays a vital role in metal removal by crab shell. For all heavy metal ions, the sorption rate was very fast with equilibrium reached around 30 min. In the case of *Sargassum*, the light metal ions were released from the biomass and thereby their concentrations in the final solution increased as the time progressed (Figure 4). Due to ion-exchange mechanism, the heavy metal ions occupied the available free binding sites. Figure 4 clearly illustrates the relationship between release of light metal ions and adsorption of heavy metal ions due to ion-exchange phenomenon.

3.4 Desorption

To investigate the feasibility of reusing the biosorbent in multiple cycles, batch desorption experiments were conducted. The desorbent medium used was 0.1 M HCl at solid to liquid ratio of 2 g/l. For metal-loaded *Sargassum* biomass, 0.1 M HCl performed well by releasing all heavy metal ions from binding sites with elution efficiencies greater than 98% for all heavy metal ions. Also, the weight loss is less than 4%. In the case of crab shell, the elutant performed well with desorption efficiencies greater than 96.5% for all examined heavy metal ions. However, the weight loss was found to be 30%. The mineral constituents of crab shell tend to dissolve under strong acidic conditions. Additional research is therefore required to identify a proper elutant for crab shell to enable its potential reuse.

4. Conclusions

This research identified two potent biosorbents for remediation of urban storm water runoff. The crab shell, in general, showed better performance with high affinity towards all heavy metal ions. The rate of metal removal was rapid with the possibility of desorption. Additional work is needed to enhance the biomass regeneration and examine the possibility in a continuous mode of operation.

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