Study of Heavy Metal Pb^{2+} and Hg^{2+} Ions Adsorption by Extracted Chitosan

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Abstract

In this research work natural bio polymer "chitosan" was synthesized using fish shells and adsorption of lead and mercury ions by chitosan were studied. Synthesize of chitosan involved three main stages, demineralization, deproteinization and deacetylation. Chitosan was characterized using Fourier Transform Infrared Spectroscopy (FTIR) and solubility in 1% acetic acid. The affinity of chitosan for lead and mercury was studied using $Pb(NO_3)_2$ and $HgCl_2$ solution as the heavy metal solutions containing Pb (II) and Hg (II) ions.

The ability of chitosan as an adsorbent for Pb (II) and Hg (II) ions in aqueous solution was studied. The capacity of chitosan to trap lead and mercury ions in aqueous solution was carried out at 30^{o}C using concentration as parameters. Our results show that the adsorption process is concentration-driven with high capacity of chitosan for the adsorption of these metals ions. The Infra red spectroscopic study on the chitosan and the metal-chitosan complexes reveal a metal coordination based on the observed characteristic band changes. At initial lead and mercury concentrations of 3, 5, 8 and 10 mg/L, the adsorbed ions concentrations were 2.7495, 4.5873, 7.4897 and 9.3648 mg/L for lead ions, and 2.8160, 4.6495, 7.2916 and 9.4551 for mercury ion.

Keywords: chitosan, heavy metal, bio-adsorption, complex.

الخلاصة

في هذا البحث تم استخلاص مادة الكيتوزان من قشور السمك و درس امتزاز ايونات الرصاص والزئبق بالمادة التي تم استخلاصها من قشور السمك بالمراحل التاليه: إزالة المعادن, إزالة البروتين , إزالة الاستايل. تم تشخيص الكيتوزان المستخلص بطيف الأشعة تحت الحمراء والإذابة بحامض ألخليك المخفف ١% .درست ألفة الكيتوزان للرصاص والزئبق باستخدام محلول نترات الرصاص وكلوريد الزئبق كمحلول يحوي ايونات الرصاص والزئبق الثنائية. تم دراسة قابلية الكيتوزان لامتزاز ايونات الرصاص والزئبق في المحلول المائي تم دراستها كذلك عند درجة ٣٠ درجة مئوية مع تغير تركيز هذين الايونين. أظهرت النتائج قابلية عالية للكيتوزان لامتزاز الرصاص والزئبق وذلك لتكوين معقدات مع هذين الايونين .تم تقدير تركيز هذين الايونين في المعقدات الناتجه والمتبقي منها في المحلول باستخدام الأشعة تحت الحمراء للكيتوزان والمعقد الناتج وتقنية الامتصاص الذري.

الكلمات المفتاحية: كيتوزان, عناصر ثقيلة, ممتز, معقد.

1. Introduction

Due to increase in the world population and development of industrial applications, environmental pollution problem became important. Communities produce both liquid and solid wastes. The liquid waste-wastewater- is essentially the water supply of the community after it has been used in a variety of applications. In recent years, heavy metal concentrations, besides other pollutants, have increased to reach dangerous levels for living environment in many regions. The presence of toxic and polluting heavy metals in wastewaters from industrial effluents, water supplies and mine waters and their removal has received much attention in recent years. The amount of heavy metals that industrial wastewaters often contain is considerable and would endanger public health and the environment if discharged without adequate treatment. Heavy metals are elements such as Cu , Cd , Ni , Pb , Zn , Ag , Cr (III) , Hg, Fe , Co , As ,which are usually associated with toxicity and natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination [WEB_1, 2007]. Lead is rarely found as the free metal in nature, but it is present in several minerals, principally in galena (PbS) the main source for lead production. It is also found as anglesite ($PbSO_4$) and cerrusite ($PbSO_3$). Lead is one of the most commonly used non-ferrous metals. It has many applications; its largest use is in making storage batteries, most of which are recycled. As a result of its resistance to corrosion and its malleability, it finds use in building constructions, storage tank lining and corrosive liquid containers. Other uses of the metal are for radiation shielding, ammunition, solder, cable sheathing and pipework. Lead compounds are used as pigments in paints and ceramics, catalysers, antibacterial substances and wood preservatives. A major use is the production of anti-knock compounds for addition to petrol, particularly tetraethyl lead, $Pb(C_2H_5)_4$. The exhausts from vehicles are a major source of the environmental contamination by lead. Lead is present in exhaust gases mainly as lead halides and oxides, but incomplete combustion results in about 10% of alkyl lead compounds also being present. Other source of lead emissions are copper and nickel smelters, iron and steel production. Estimates vary as to the importance of vehicle emissions as the source of the lead contamination. Lead exist in the oxidation states Pb^{2+} and Pb^{4+}, with the divalent form being the more stable in most aquatic environments. The speciation of lead compounds in water is complicated and depends upon a number of factors, principally pH, dissolved oxygen and the concentration of other organic and inorganic compounds. In surface waters, lead is presents as hydrated Pb^{2+}, or $[PbCO_3\,(aq)]^0$ in the pH range 7-9. At pH 6, Pb^{2+} and $Pb(OH)^+$ are in equal concentration, whereas at higher pH values there is an increase in Pb in form of $Pb(CO_3)_2\,^{2-}$, $Pb(OH)^+$ and concentration of lead in waters is usually limited by the solubility of PbCO3, and by its adsorption onto particulate matter [Dojlido and Best, 1993; Trivedi, *et al.*, 2001]. Heavy metals are released into the environment by activities of people and high levels of these metals constitute a great risk for the aquatic ecosystem and human [Kurniawan, *et al.*, 2006]. Chitosan is a natural carbohydrate biopolymer derived by deacetylation (DA) of chitin, a major component of the shells of crustacean such as crab, shrimp, and crawfish figure (1). After cellulose, chitin is the second most abundant natural biopolymer found in nature [No, & Meyers, 1989]. Chitosan is a non-toxic, biodegradable and biocompatible polymer. Over the last several years, chitinous polymers, especially chitosan, have received increased attention as one of the promising renewable polymeric materials for their extensive applications in the pharmaceutical and biomedical industries for enzyme immobilization and purification, in chemical plants for wastewater treatment, and in food industries for food formulations as binding, gelling, thickening and stabilizing agent [Knorr, 1984]. Due to increase in the world population and development of industrial applications, environmental pollution problem became important.

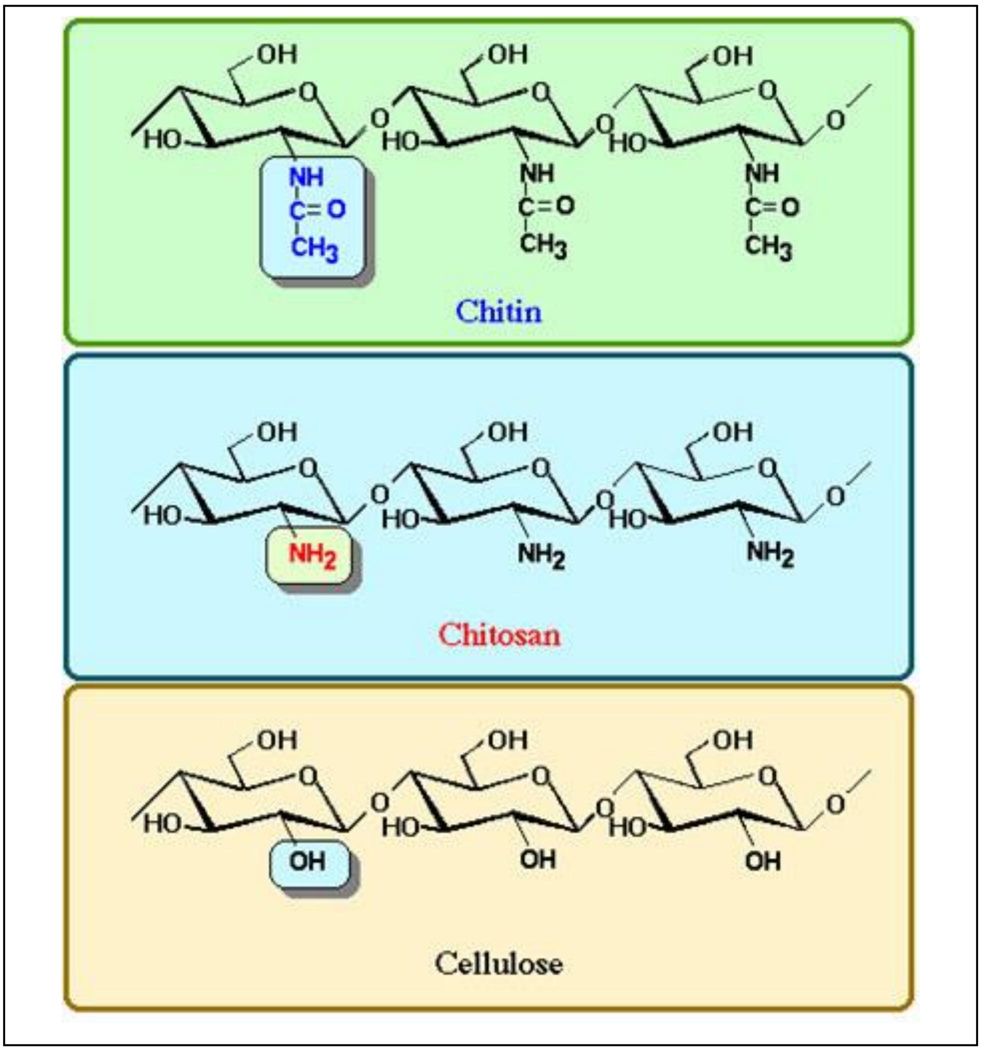


Figure 1. Chemical structures of chitin, chitosan and cellulose[7].

The overall objective of this study is to investigate the lead and mercury removal from wastewater by adsorption using chitosan. The specific objectives included; extracted chitosan from fish shells and removal of lead and mercury ions using as a bio-adsorption material.

***Apparatus*;** FTIR-8400S Shimadzu, Japan.

Atomic absorption spectroscopy,AA-6300 Shimadzu, Japan.

2 Materials and Methods

2.1 Crawfish Chitosan Production

2.1.1 Raw Material

Crawfish shells were obtained from a commercial crawfish shells were separated, and washed carefully under running tap water to remove soluble organics, proteins and other impurities, and then they were dried.

2.1.2 Isolation of Chitosan

1) DP (Deproteinization)

The crawfish shells were deproteinized with 3 % (w/v) NaOH solution for 1 hr at b.p^{o}C with constant stirring at a solid to solvent ratio of 1:10 (w/v) [No & Meyers, 1989]. The poiled sample was removed from hot plate and placed in hood then allowed to cool at room temperature for 30 minutes. Samples were then filtered under vacuum, and the filtrate was washed with tap water for 30 minutes and oven-dried (80^{o}c).

2) DM (Demineralization)

Depending upon the production sequence, the crawfish shells or deproteinized shells were demineralized with 1N HCl for 60 min at room temperature with a solid to solvent ratio of 1:25 (w/v) [No & Meyers, 1989], and then filtered under vacuum. The filtrate was washed for 30 min with tap water and oven-dried.

٣) Deacetylation

Deacetylation is the process to convert chitin to chitosan by removal of acetyl group. It is achieved by treatment with concentrated sodium or potassium hydroxide solution 50% at 90^{o}C or higher for 2hours to remove some or all of the acetyl groups from the polymer [No & Meyers, 1989; WEB_4, 2007; Muzzarelli, 1977]. The N-acetyl groups cannot be removed by acidic reagents without hydrolysis of the polysaccharide, thus, alkaline methods must be employed for N-deacetylation [Muzzarelli, 1977].

2.1.3 Sorption of Pb^{2+} and Hg^{2+} ions on chitosan

20 ppm lead and mercury solutions were prepared by dissolving 33 and 34 mg analytical grade $Pb(NO_3)_2$ and $HgCl_2$ powder respectively in distilled water. These solutions were kept as stock solution and 3, 5, 8 and 10 ppm solutions were prepared by diluting stock solution.

50ml of 3ppm $Pb(NO_3)_2$ solution was taken and 50mg of chitosan was added. Then the mixture was continuously stirred using magnetic stirrer for 2 hours at (30 ^{0}C). After that solution was filtered and 3ppm $Pb(NO_3)_2$ of the filtrate solution were analyzed using atomic absorption spectroscopy to determine amount of lead absorbed by chitosan. The same steps were repeated to the other dilute solutions. Also the same procedure was repeated to $HgCl_2$ solution.

Finally uptake of lead and mercury by amine groups ($-NH_2$) on chitosan was investigated using FTIR spectroscopy (Bruker Alpha-T) in the range of 400 to 4000 cm-1.

3. Results and Discussion

Table (3-1). The results of the adsorption of lead and mercury ions after addition of 50mg of chitosan at 30^{o}C and pH6.

Total Pb^{2+} and Hg^{2+} in original solution(mg/L)	Total adsorb $^{Pb2+}$ after chitosan addition mg/L	Total adsorb Hg^{2+} after chitosan addition mg/L
3	2.7495	2.8160
5	4.5873	4.6495
8	7.4897	7.2916
10	9.3648	9.4551

Table (3-2). Adsorption percentages of lead and mercury ions adsorbed after adding 50mg of chitosan.

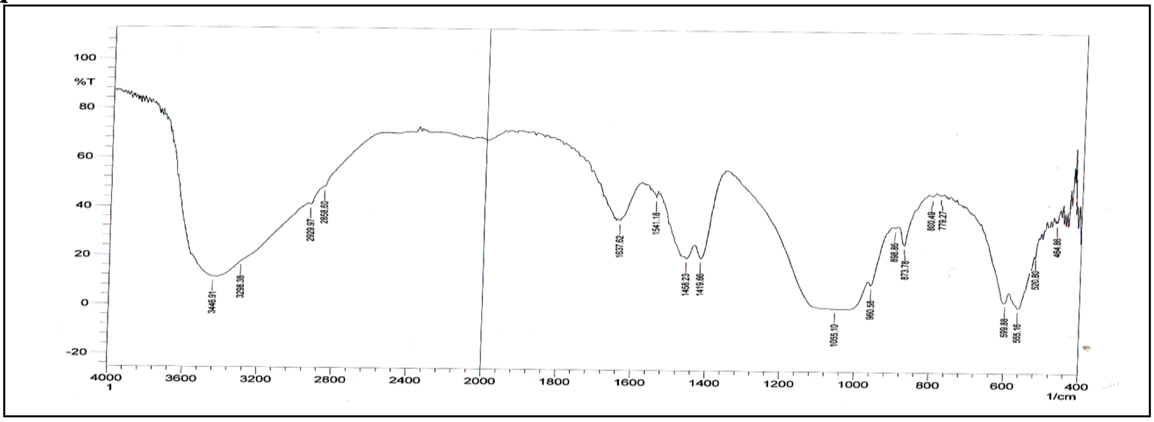
Total Pb^{2+} and Hg^{2+} in original solution(mg/L)	Adsorption % of Pb^{2+}	Adsorption % of Hg^{2+}
3	91.65	93.866
5	91.746	92.99
8	93.621	91.145
10	93.648	94.551

From the above table it's appeared that the adsorption process was increased by increasing the lead and mercury ions concentration [Angham, 2012]

FT-IR analysis

The spectra of chitin, chitosan, chitosan-Pb and Hg polymeric complexes are shown in Figure 2. The band amide (C=O) around 1637 cm^{-1} stretching frequency, characteristic of chitosan with acetylated units is present in all the spectra. However, in chitosan-metal complexes, a new band around 1625-1635 cm^{-1} appears. These bands correspond to the bending in plane of N-H which also appears as a shoulder at around 1605 cm^{-1}, this observed red shift is due to interaction of chitosan with the metal ions. The broad bands in the region 3000-3600 cm^{-1} could be attributed to the stretching of OH groups of the chitosan and overlapping stretching bands of NH. With the chitosan-metal complexes, the bands are unfolded and the stretching of O-H is observed between 3418 and 3450 cm^{-1} while the stretching of N-H is observed between 3260 and 3266 cm^{-1}. In presence of metal ions, the band shifted and appear between 1113 and 1116 cm^{-1} which correspond to the stretching of C-O bond of C3 from chitosan (secondary OH, Figure 1) as well as the band between 1025 and 1030 cm^{-1} corresponding to the stretching of C-O bond of C6 from chitosan (primary OH) verifying the complexation of the chitosan to Pb not only via the amine groups, but also through the OH groups [Duarte *et al.*, 2001]. Also in this region, two important bands were identified in the chitosan-metal polymeric complexes. The stretching frequencies between 1064 and 1075 cm^{-1} correspond to the asymmetric stretching of C-O bonds.

a-



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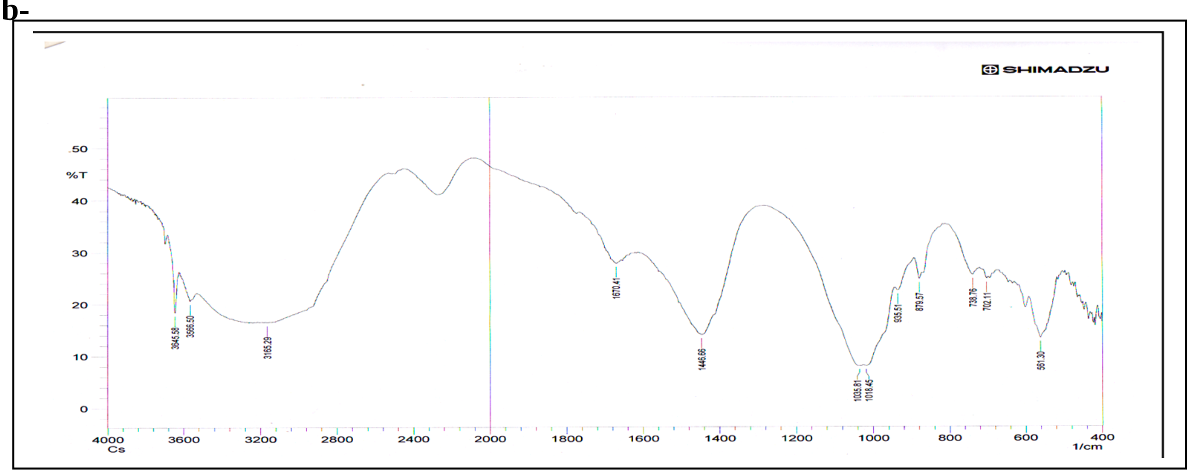

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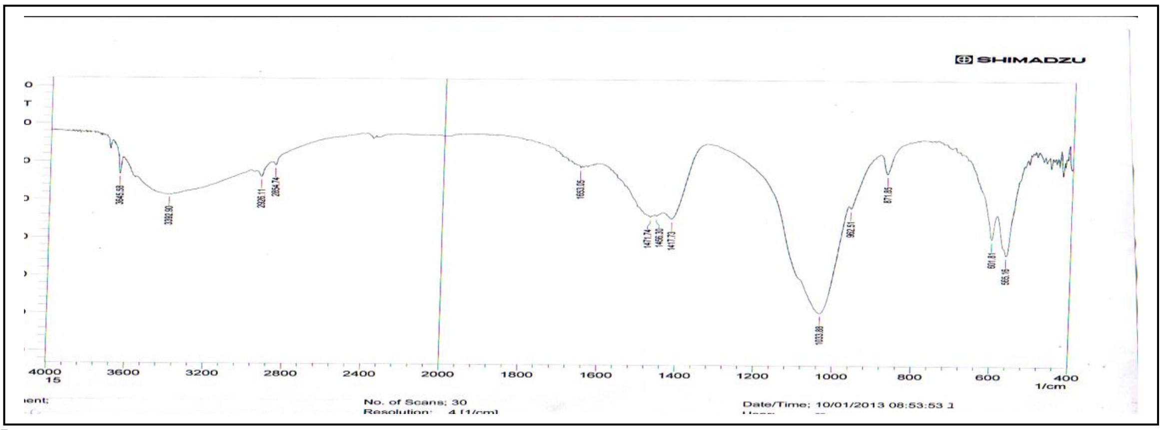

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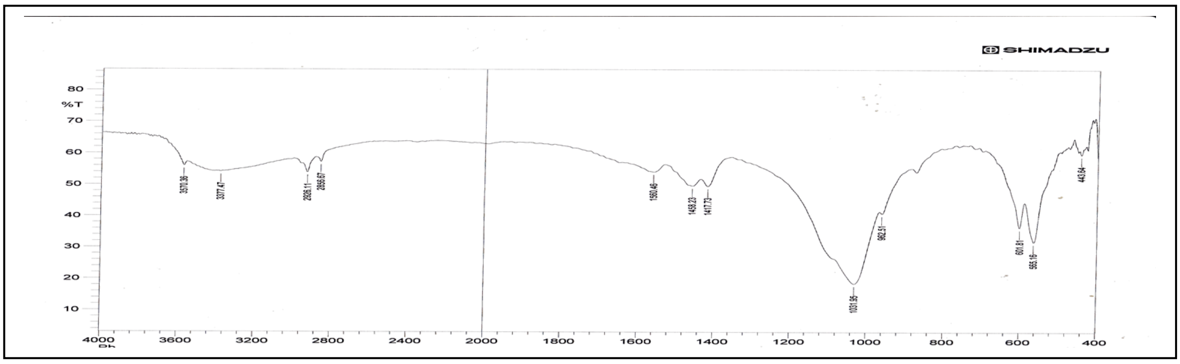

Figure 2. FT-IR Spectra of a: Chitin, b: Chitosan, c: Chitosan-Hg complex and d: Chitosan-Pb complex.

Conclusions

This study showed that chitosan adsorbs heavy metals, in particular Pb (II) and Hg (II) ions. Chitosan as a result of its bioavailability would be economically useful for the treatment of wastewater containing heavy metals.

Recommendation

1. Affection study for the application of chitosan on other heavy metals.
2. Optimization mox doze of heavy metal, with high removal efficiency.

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