Continental J. Applied Sciences 10 (2): 1 - 12, 2015
© Wilolud Journals, 2015
Printed in Nigeria

ISSN: 1597 – 9928
http://www.wiloludjournal.com
doi:10.5707/cjapplsci.2015.10.2.1.12

RESEARCH PAPER

ADSORPTION STUDY OF LEAD (II) FROM AQUEOUS SOLUTION BY MODIFIED AND UNMODIFIED CHITOSAN

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ABSTRACT

This research work presents a comparative study in the application of chemically modified and unmodified chitosan for the removal of lead (II) from aqueous solution. The effect of pH and initial metal concentration were investigated using the batch method. The highest sorption percent removal observed for unmodified chitosan (UC) is 46.35%, while that of Modified chitosan (MC) is 80.37%. The initial metal concentration decreased from 71.92% to 40.23%, and 44.38 to 33.45% for modified and unmodified chitosan respectively. The adsorption equilibrium data fitted Langmuir model better than Freundlich models. Typical macro reticular structure with spherical primary particles of about 3 µm was observed only in the SEM micrograph of modified chitosan. The results from this study revealed that modified chitosan could be used as an effective adsorbent material for the removal of Pb (II) in aqueous solution

KEYWORDS: Chitosan, chitin, lead (II) and prawn.

Received for Publication: 10/06/15 Accepted for Publication: 01/09/15
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INTRODUCTION

Removal of heavy metals from water system has been a challenge for a long time owing to their environmental harm and threat to life (Mohamed, Moustafa, Mohamed, Elblbesy and Bothaina, 2011).

Lead is one of the most significant heavy metal toxins. It's concentration in many industrial effluents regularly exceed the World Health Organization limit of $0.05mgl^{-1}$, the Standard Organization of Nigeria limit is $0.1mgl^{-1}$ (Ogwuebgu and Muhnga, 2005). Lead poisoning causes inhibition of the synthesis of heamoglobin; dysfunctions in the kidney, joints and reproductive systems, cardiovascular system and acute and chronic damage of the central nervous system (CNS) (Underwood, 2002).

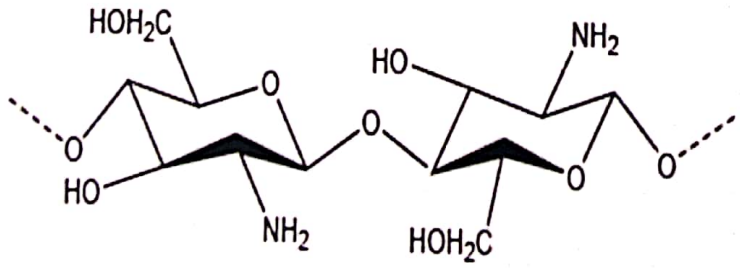
A number of conventional methods used to remove heavy metals include chemical precipitation, ion exchange, electro dialysis, membrane separation, reverse osmosis, and solvent extraction (Mohamed et al., 2011). However, these conventional technologies appear to be inadequate and expensive, have resulted in the search for alternative methods that would be efficient for metal sequestering. One of such methods is the use of sorbents based on metal binding capacities of various biological materials of little or no cost (Annadurai, Ling and Lee, 2008).

Chitin and its deacetylated derivative chitosan are natural polymers composed of randomly distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit) (Hudson and Jenkins, 2001). One of the earliest applications of chitosan was to chelate harmful metal ions such as copper, lead, mercury, and uranium from waste water. Studies on the chelation property have been documented by many scientists (Duck, Hosun, Chong and Woo, 2009). The investigation of the chelation ability of chitin and chitosan was reported (Nwe, Furuike and Tamura, 2010) that chitosan exhibited the best chelation of transition metal ions. This is explicable in terms of the polymer's high *N*-amino group content, which acts as electron rich donors. New et al. (2010) assessed the chelating ability of chitosan-glucan, which is derived from alkaline treatment of waste mycelia of *Aspergillus niger*. Chitosan-glucan exhibited selective adsorption of Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} from solution.

A study of the metal binding capacity of chitosan has shown that it has a high binding capacity with metals such as copper and vanadium (Rinaudo, 2006).

The use of commercially available chitosan for potable water purification has been approved by the United States Environmental Protection Agency (USEPA) up to a maximum level of 10 mg/L (Tan et al., 2008).

However, in the real applications in wastewater treatment, chitosan has different degrees of limitations which includes; unsatisfactory mechanical properties, poor heat resistance, dissolution in acidic media, high swelling ratios, and limited adsorption capacities for some metal ions (Benavente, 2008). These could be overcome by modification such as grafting and cross linking.



Structure of Chitosan (Monarul, 2011).

Aim and Objectives of Study

The objectives of this work are to investigate the possibility of using modified chitosan extracted from prawn shells for the removal of Lead (II) from aqueous solution and to make a comparative study of the adsorption potential of the modified and unmodified chitosan and evaluation of the efficiency of the adsorbents.

MATERIALS AND METHODS

Samples Collection

Dried prawns were purchased from Gwagwalada Market, Abuja. The exoskeletons (i.e the heads, shells and tails) were separated from the meats for chitin and chitosan extraction.

Preparation of Unmodified Chitosan (UC)

All the chemicals used were of analytical grade. Chitin and chitosan were prepared from prawn shell according to Gopalakannan, Indra, Shanmugam and Sugumar (2000) method with some modifications. Dried shells waste were washed with tap water and deproteinised by boiling in100ml of 5% aqueous sodium hydroxide for 5h. After draining the alkali, the process was repeated for the removal of residual protein from the shell and washed with tap water. The deproteinised shell was demineralised by 100ml of HCl (1.25 M) at room temperature for 5 h. The acid was drained off and washed thoroughly with tap water followed with distilled water. The chitin was dried at temperature of 30°C in the oven. The chitosan was prepared by deacetylation of chitin by treating with 100ml of 50% aqueous sodium hydroxide at 90°C – 95°C for 48 h. After deacetylation the alkali was drained off and washed with tap water followed by distilled water. Finally, the chitosan was dried in the oven at $30^{o}C$.

Preparation of Modified Chitosan (MC)

The suspension cross-linking technique was used for the preparation of modified chitosan (Doan, Tran, Le Hong, Bui, Le Khanh and Phan, 2009). In this procedure, 5% chitosan solution was prepared using a 2% aqueous acetic acid solution containing 0.2 g Fe_3O_4 dry magnetic particles. After which the solution was poured, drop-wise, into the dispersion medium, compose of 30 ml paraffin and 0.5 ml span-80. During this process, the dispersion medium was stirred with a strong ultrasonic agitation at room temperature. Next, an additional 3ml of 25% glutaraldehyde solution was added to the dispersion medium and the solution was stirred for further 5 h using a mechanical stirrer. At the end of this period, the chitosan-magnetite composite particles were recovered from the reaction mixture by using a permanent magnet; then the products were washed with ethanol and dry in a vacuum oven at $110^{0}C$ for 2 days.

Effect of pH

Effect of pH on the removal of metal ions from aqueous solution was studied by adding 5.0mg each of the adsorbent into different 250 ml conical flask containing 50 ml of metal solution, initial concentration being 100mg/l for Pb(II) solution. The pH meter Thermo Orion (Model 420A+) was used for the analysis and the samples were adjusted to different values: 2,3,4,5,6,8,9,10 and 12 using 0.1 mol dm^{-3} NaOH and 0.1 mol dm^{-3} HNO_3.

Adsorption Experiment

The studies were conducted using a batch technique. The reactor for the equilibration reaction was basically 250 ml corked conical flask which holds 50ml of the working concentration. The pH of the solution was adjusted with 0.01mol dm^{-3} NaOH and 0.01mol dm^{-3} HNO_3. The reactor content was mechanically agitated in a thermostat shaker water bath for 180 minutes at 120 rpm. The contact experiment was done in triplicates and the reactor contents were separately filtered into sample bottles using Whatman No 1 filter paper. A Bulk Scientific 2000 model Analytical Atomic Spectrophotometer was used to determine the metal ions concentration in the solution before and after the experiment.

RESULTS AND DISCUSSION

The highest sorption percent removal observed is 46.35% for unmodified chitosan (UC), while that of Modified chitosan (MC) is 80.37%.

For unmodified chitosan (UC), it was observed the Percentage removal of Pb (II) increased from 23.56% to 46.35% as pH increases from 2.0 to 5.0 and decreased to 40.34% at pH 6.0.

The percentage removal observed in modified chitosan increase from 44.87% to 80.37% as pH increases from 2.0 to 5.0 and decreased to 60.21% at pH 6.0

The increase in Pb (II) removal as pH increases can be explained on the basis of a decrease in competition between proton and the metal cation for the surface sites and by the decrease in positive surface charge, which results in a lower coulombic repulsion of the sorbing metal cation (Dianati-Tilaki, Mahvi, Shariat, and Nasseri, 2004). Leyva, Rangel, Mendoza, Fuentes and Guerrero, (1997) reported similar result for the adsorption Cd (II) onto activated carbon. At pH below 7, the Pb^{2+} ion predominates and pH values just below 9, the metal ion begins to precipitate out as their hydroxides (Dianati-Tilaki *et al.*, 2004).

Reduction in percentage removal of Pb (II) at lower pH value is attributed to repulsion between positively charged adsorbents surfaces and positive metal ions. It has been reported that at low pH values in aqueous medium, surfaces of adsorbents are closely associated with H_3^+O (Low, Lee and Lee, 1995) which hinders the access of metal cations, by repulsive forces, to the surface functional groups and consequently decreasing the percentage metal removal.

Futhermore, the decrease in percentage removal at pH value greater than 6 is attributed to the formation of insoluble metal hydroxides (Nomanbhay and Palanisamy, 2005).

Table 1: Effect of pH of solution on adsorption of Pb(II) ion unto modified chitosan (MC) and unmodified chitosan (UC).

pH	Initial Conc. (mg/l)	Final Conc. (mg/l)	MC Adsorbed (%)	Initial Conc. (mg/l)	Final Conc. (mg/l)	UC (%) Adsorbed
1	100	62.58	37.42	100	85.88	14.12
2	100	55.13	44.87	100	76.44	23.56
3	100	55.52	44.48	100	72.33	27.67
4	100	41.29	58.71	100	63.46	36.54
5	100	19.63	80.37	100	53.65	46.35
6	100	38.79	61.21	100	59.66	40.34
7	100	43.29	56.71	100	54.34	45.66
8	100	61.66	38.34	100	54.33	45.67
9	100	61.59	38.41	100	66.32	33.68

The effect of initial concentration

The metal uptake mechanism depended on the initial metal ion concentration. From this study, the metals were absorbed by specific sites at low concentrations. But the adsorption amount did not increase proportionally for higher metal ion concentrations since the active sites were filled and saturated. Hence, it was very clear that the percentage removal of metal ion decreased with increase in metal ion concentration. This was also reported by Thilagan, Gopalakrishnan and Kannadasan; 2013.

For modified chitosan (MC) the removal of Pb(II) ions decreased from 71.92 % to 40.23 %, and that of unmodified chitosan (UC) decreased from 44.38 % to 33.67 %. The decrease in percentage adsorption can be attributed to lack of sufficient surface area to accommodate more metal ion available in the solution as the concentration increases. At lower concentrations, all metal ions present in solution could interact with the functional group and binding sites on the surface of the adsorbent and thus the percentage adsorption was higher than those at higher metal ion concentrations. At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites.

Adsorption isotherm

The results obtained for the effect of concentration were analyzed using adsorption isotherms. Langmuir and Freundlich isotherms were the adsorption isotherm employed for interpretation of adsorption data obtained. Adsorption isotherms are characterized by certain parameters (qe, Ce, Ce/qe, logCe, logqe, qmax), the values of which express the surface properties and affinity of the adsorbent towards the adsorbate and can also be used to find the maximum adsorption capacity of the adsorbents. Where qe is the equilibrium adsorption capacity of the adsorbent (mg/g), Ce is the equilibrium metal ions concentration in solution (mg/l), qmax is the maximum amount of metal ions that could be adsorbed on the adsorbent (mg/g).The plot of Ce/qe versus *Ce* illustrates the linearised form of Langmuir model while the plot of the plot of logqe versus logCe illustrates the linearised form of Freundlich model (Thilagan *et al.*, 2013).

Table 2: Effect of Initial concentration on the adsorption of Pb (II) ion unto modified chitosan (MC) and unmodified Chitosan (UC).

Time (min)	Initial Conc. (mg/l)	Final Conc. (mg/l)	MC Adsorbed (%)	Initial Conc. (mg/l)	Final Conc. (mg/l)	UC (%) Adsorbed
60	25	7.02	71.92	25	13.91	44.38
60	50	22.32	55.36	50	31.67	36.67
60	75	34.76	53.65	75	52.16	30.45
60	100	54.13	45.87	100	66.55	33.45
60	125	74.71	40.23	125	82.91	33.67

Adsorption equilibrium data are fitted much better to the Langmuir isotherm, compared to the Freundlich isotherm model.

Fig 1 to 2 show the Langmuir isotherm at different temperature for Pb (II) ion adsorption onto modified chitosan and unmodified chitosan.

For modified chitosan and unmodified chitosan, Langmuir isotherm fitted at 308K than 293K and 318K.

Fig 3 to 4 displayed the Freundlich isotherm at different temperature for Pb (II) ion adsorption on to modified chitosan and unmodified chitosan. It can be observed that the illustration was not fitted when compared to Langmuir isotherm.

Table 3 summarized the constants of the isotherms and their corresponding correlation coefficient (R^2) at different temperature for the adsorption of Pb (II). Examination of the Figures and correlation coefficients in Table 1 to 2 showed that the Langmuir model was more applicable to the adsorption of Pb (II) by the adsorbents used than Freundlich model. The Langmuir constants K_L and q_m which are related to the affinity between the adsorbent and adsorbate and adsorption capacity were found to increase with increasing temperature for all the adsorbents used. This indicated that the adsorption processes involved more heat of adsorption and increased adsorption capacity for the adsorbent with increasing temperature (Moharptara, Khatun and Anand, 2009).Thus, according to (Soon-An, Eiichi, Makoto and Tadashi, 2010) report, the process involved in this, is an endothermic process.

This showed that adsorbate-adsorbent interaction was greater than adsorbate-adsorbate interaction as the temperature of the system is increased. Therefore, the extent of adsorption of the metal ions increased with increasing temperature confirming the endothermic nature of the processes (Mohapatra *et al.*, 2009).

The results obtained with the Freundlich isotherm show that the values of K_F increased with the increasing temperatures indicating increased affinity of the adsorbent for the metal ions

(Kushwaha, Sodaye and Padmaja, 2008). It also reflected increased adsorption capacity for the adsorbent and confirmed the endothermic nature of the processes (Aslam, Alam and Rais, 2009). The 1/n values were between 0 and 1 indicating that the adsorption of the metal ions onto the adsorbents used was favorable at studied conditions (Kushwaha *et al.*, 2008). When $1/n = 0$, it shows that the partition between adsorbate liquid and the adsorbent does not depend on the concentration of the adsorbate, $1/n < 1$ corresponds to a normal L-type Langmuir isotherm while, $1/n > 1$ indicates a cooperative sorption involving strong interactions between the molecules of adsorbate (Kiran, Maria, Zobia, Hameed, Fauzia and Rani, 2010). Thus, the adsorption isotherms obtained in this study are L-type Langmur isotherm and this is a characteristic for strong chemical interactions (Yavuz, Guzel, Aydin, Tegin and Ziyadanogullari, 2007).

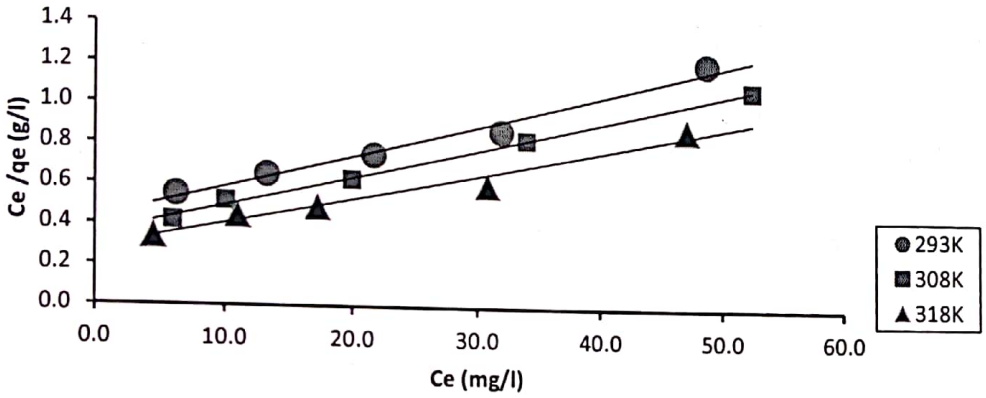


Fig.1 Langmuir isotherm at different temperature for Pb(II) ion adsorption onto Modified Chitosan (MC).

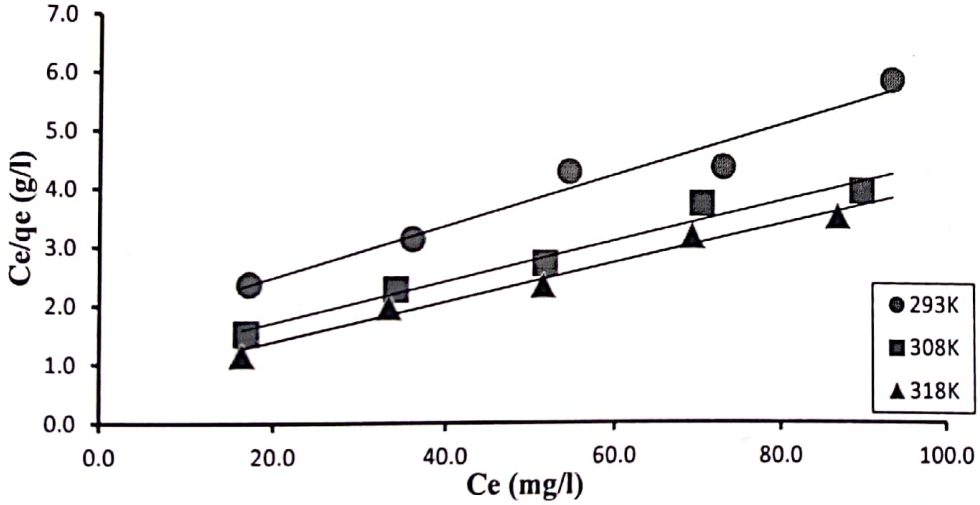


Fig.2 Langmuir isotherm at different temperature for Pb(II) ion adsorption onto Unmodified Chitosan (UC).

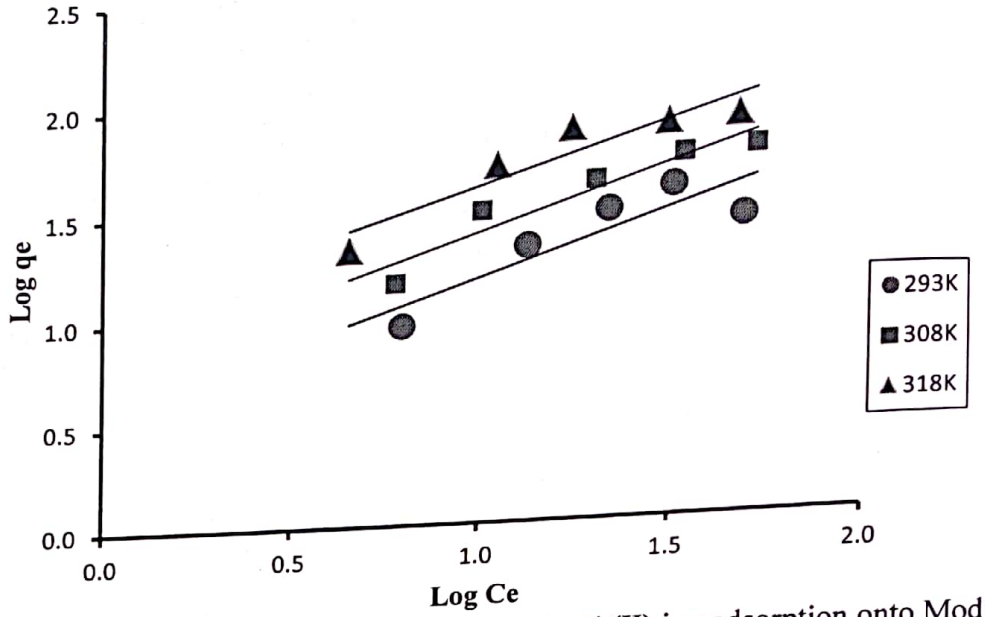


Fig.3 Freundlich isotherm at different temperature for Pb(II) ion adsorption onto Modified Chitosan (MC).

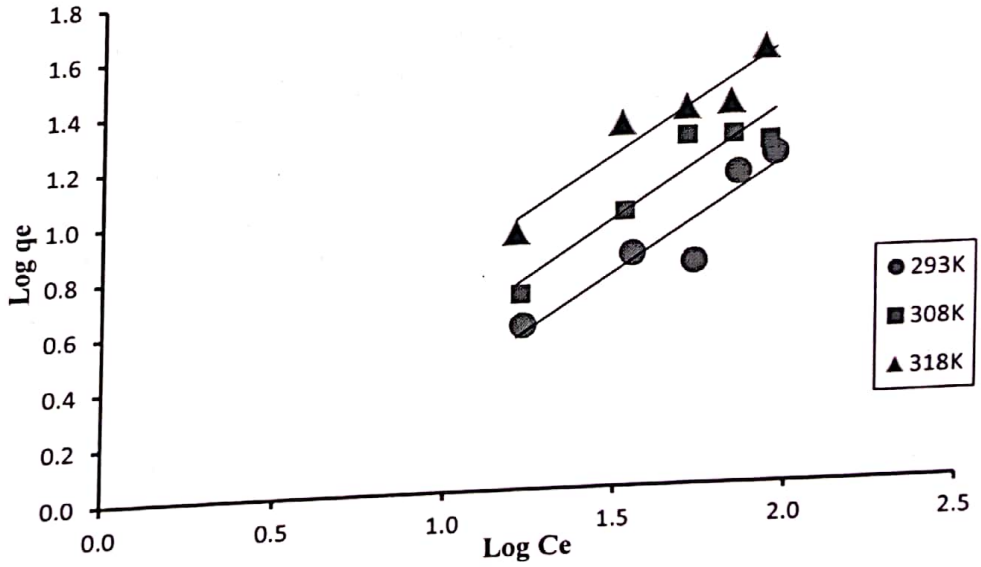


Fig.4 Freundlich isotherm at different temperature for Pb (II) ion adsorption onto Unmodified Chitosan (UC)

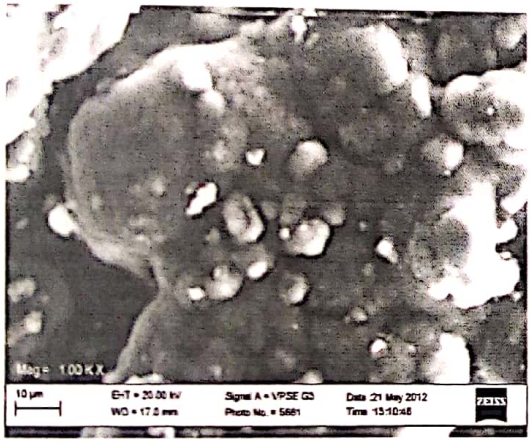
Table 3: Langmuir, and Freundlich isotherms constants and correlation coefficients for Pb (II) adsorption unto unmodified chitosan and modified chitosan.

	Modified Chitosan			Unmodified Chitosan		
Temperature	298K	308K	318K	298K	308K	318K
Langmuir						
q_m(mg/g)	64.94 ± 0.01	72.61 ± 2.32	78.13 ± 0.61	24.18 ± 1.86	27.71 ± 0.54	32.42 ± 2.92
K_L (L/mg)	0.032 ± 0.00	0.036 ± 0.01	0.040 ± 0.01	0.017 ± 0.01	0.024 ± 0.01	0.027 ± 0.01
R^2	0.986 ± 0.00	0.960 ± 0.04	0.984 ± 0.01	0.963 ± 0.01	0.978 ± 0.01	0.989 ± 0.01
Freundlich						
K_F (mg/g)	3.457 ± 0.60	6.023 ± 0.55	9.970 ± 1.82	0.387 ± 0.02	0.583 ± 0.02	1.146 ± 0.08
1/n	0.635 ± 0.06	0.577 ± 0.01	0.536 ± 0.00	0.819 ± 0.01	0.773 ± 0.01	0.759 ± 0.01
$*R^2$	0.815 ± 0.08	0.879 ± 0.00	0.872 ± 0.03	0.895 ±0.02	0.903 ± 0.01	0.913 ± 0.00

Note: R^2 and $*R^2$ are the correlation coefficients of Langmuir and Freundlich isotherms respectively

SEM image of modified and unmodified chitosan

Plate A and B shows typical SEM micrographs of modified and unmodified chitosan respectively. Typical macro reticular structure with spherical primary particles of about 3 µm was observed in modified chitosan. This is caused by a simultaneous suspension crosslinking. This is similar to the pattern obtained by Kazuharu, Zhengrong and Katsutoshi,(2000), in their study of Silver-complexed chitosan microparticles for pesticide removal.



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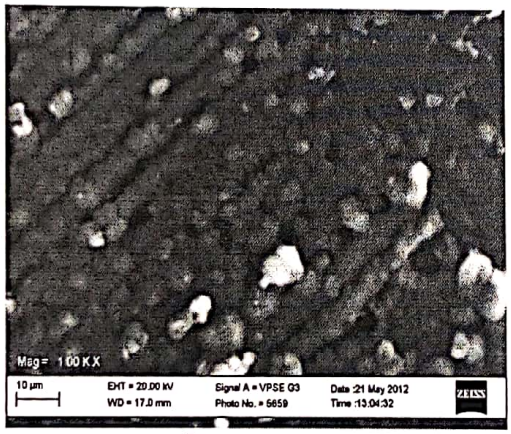

B

CONCLUSION AND RECOMMENDATION

Conclusion

The results of this study revealed that Modified Chitosan could be used as an effective adsorbents material for the removal of Pb(II) from aqueous solution. The adsorption of the metal ions onto adsorbents used was found to be concentration and pH dependent. Maximum percentage removal occurs between the pH range of 5.0 to 7.0 for Pb(II) ions and the adsorption equilibrium data fitted Langmuir model better than Freundlich models.

RECOMMENDATION

Chemical modification of chitin and chitosan improved their solubility in water or organic solvents, which also enhance their biological activities and allow the continuous development of their applications as functional biomaterials with excellent potential in various fields.

In order, to have a deeper understanding of the mechanism of their properties, it is necessary for chitin/chitosan and their derivatives to be structurally and physicochemically well characterized. Knowledge of the microstructure of these compounds is essential for an understanding of structure–property–activity relationships.

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