RASĀYAN J. Chem.
Vol. 9 | No. 4 |680 - 685 | October - December | 2016
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

TELESCOPE SNAIL (*Telescopium* sp) AND MANGROVE CRAB (*Scylla* sp) AS ADSORBENT FOR THE REMOVAL OF Pb^{2+} FROM AQUEOUS SOLUTIONS

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ABSTRACT
The present study was conducted to determine the pontential of telescope snail and mangrove crab shell powder as metal ions Pb^{2+} adsorbent. In addition, evaluate the effectiveness of them for the removal of Pb^{2+} from aqueous solutions. The evaluation include equilibrium adsorption time, adsorption capacity, functional groups, surface structure and substances formation of adsorbents. This study was conducted in laboratory scale using the batch method. Adsorption with variation contact time was performed into Pb^{2+} solutions as synthetic waste water. The results of metal ions Pb^{2+} adsorption in solutions measured by AAS. The analysis results showed both of kind adsorbents reached adsorption equilibrium time on 120 minutes with adsorption capacity 9.93 mg g^{-1} for telescope snail shell powder and 9.50 mg g^{-1} for mangrove crab shell powder. The results of FTIR analysis showed that functional groups of telescope snail shell powder dominated by carbonates, while the functional groups of mangrove crab shell powder obtained typical compound of chitin and carbonate. Based on the results of this study, telescope snail and mangrove crab shell wastes can be used for the removal of Pb^{2+} from aqueous solutions.

Keywords: adsorption capacity, equilibrium adsorption time, Pb^{2+}, *Scylla sp., Telescopium sp.*

INTRODUCTION

Rapid industrialization development has occurred over a short period of time, resulting in heavy metal contamination of aquatic system. One of heavy metal contaminants are lead (Pb). The presence of Pb in the environment suspected caused by industry waste water disposal. Pb accumulated because of their non-biodegrability, mobility and toxicity. Pb often used widely in the chemical industry, such as the battery manufacture industrial, as covering cable material on the power cords manufacture industrial, as anti-fouling on the paint industry, explosives, ceramics glazing, flame retardants materials and additives to fuel vehicles.[1] Exposure of materials that have been contaminated with Pb can cause various health problems, namely neurological disorders, renal function, reproductive system, and anemia. It can be said that the symptoms of anemia are the early symptoms of lead poisoning in humans.[2] The content of heavy metal contaminants caused the industry have to process the waste before it is discharged into water bodies. Meanwhile, wastewater treatment requires fairly high cost. Therefore, the need for alternative treatment that was capable of removing contaminants contained in the waste water at lower cost. One effort to overcome Pb contamination in the aquatic environment that often used was the adsorption technique. Adsorption technique chosen with the advantage, that the costs involved were relatively low and does not cause toxicity.

Indonesian people who live in coastal areas utilize telescope snail and mangrove crab as food source. In addition to good taste, had high nutrition content.[3,4] Moreover, its shell has not been utilized. Not to utilization of telescope snail and mangrove crab shell were considered less valuable due to economical.

In the field of environment, chitin was used as a natural adsorbent that was able to bind pollutants in industrial wastewater, especially heavy metals.[5] Crabs, shrimp and lobster has long been known as a source of chitin production base because of its content ranges between 20-50%. In addition, there is also the shell molluscs, such as snails, clams and snails.[6] Besides chitin, calcium carbonate can also be used to adsorb heavy metals.[7] Therefore in the present study was conducted to determine the pontential of telescope snail and mangrove crab shell powder as metal ions Pb^{2+} adsorbent. In addition, in this study was also evaluated the effectiveness of them for the removal of Pb^{2+} from aqueous solutions.

EXPERIMENTAL

Materials and research equipment

Materials used in this study are telescope snail shells, mangrove crab shells, $Pb(NO_3)_2$, HNO_3 solutions 0.1 M and filter paper.The equipment used in this study are stone pounder, 80 mesh and 100 mesh sieve, aluminium tray, oven (Memmert), Ohaus balance, spatula, volumetric flask 1.000 ml (Pyrex), glass bottle, pipette, graduated cylinder 100 ml (Iwaki), shaker (Lab Tech), buchner funnel, filtering flask (Herma), vacuum pump (Gast), AAS instrument (Shimadzu AA-7000), FTIR instrument (Shimadzu prestige 64), and SEM-EDX instrument (Hitachi).

Preparation of telescope snail and mangrove crab shell powder as adsorbent

Telescope snail and mangrove crab shell are separated from the rest of meat still attached beforehand. Then, the shell is washed until clean and dried with exposure of sunlight. After that, crushed shells by stone pounder into powder. To obtain uniform powder size, the result of grinding shell sieved with criteria to pass through 80 mesh sieve and retained on 100 mesh sieve. Before use the powder was put on aluminium tray and bake in oven for 1 hour at temperature of 100˚C to obtain dry powder.

Adsorption test

Synthetic waste water were prepared by dissolving the appropriate amounts of lead nitrate ($Pb(NO_3)_2$) with the initial consentration was set at 100 mg L^{-1}. Synthetic waste water by volume of 25 ml put in a glass bottle. Then, the adsorbent added 0.25 g. Furthermore, the solution had been shaken using shaker with 100 rpm speed at room temperature. Shaking conducted according predetermined time. After that, the filtered solutions pass through buchner funnel previously installed filter paper, accommodated inside filtering flask, and assisted with vacuum pump. Screening aims to separate the adsorbent and waste water to be analyzed. For preservation and prevent chemical changes occur, the water sample was added 2 drops of HNO_3 with pipette. Then, analyzed by SSA to determine the concentration of Pb^{2+} remaining in the synthetic waste solutions.

Determination of adsorption capacity

Adsorption capacity calculated based on following equation-

$$q_e = \frac{V(C_0 - C_e)}{m}$$

Where, q_e is adsorption capacity (mg g^{-1}); *V* is volume of solutions (L); *Co* is initial consentration solutions (mg L^{-1}); *Ce* is remain consentration solutions (mg L^{-1}); and *m* is mass of adsorbent (g).[8]

Functional group, surface structure, and substance formation analysis of adsorbent

The functional groups of mangrove conch and mangrove crab shell powder after adsorption were determined by Fourier Transform Infrared (FTIR) Spectroscopy. Additionally, the surface structure and substances formation of mangrove conch shell powder was analyzed by Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX).

RESULTS AND DISCUSSION

Equilibrium time of adsorption based on adsorption capacity

Adsorption capacity of telescope snail and mangrove crab shell powder was calculated through the measurement of concentration of metal ions Pb^{2+} remaining after adsorption process for a predetermined time, namely 30, 60, 90, 120, 150 and 180 minutes. Adsorption capacity shown at Table-1.

Table-1: Adsorption capacity of telescope snail and mangrove crab shell powder

Contact Time (minutes)	Adsorption Capacity (mg g^{-1})	
	Telescope Snail (*Telescopium sp*) Shell Powder	Mangrove Crab (*Scylla sp*) Shell Powder
30	8.21	8.82
60	9.19	9.08
90	9.59	9.42
120	9.93	9.50
150	9.94	9.50
180	9.91	9.42

Based on data at Table-1, although adsorption capacity of telescope snail shell powder was less than mangrove crab shell powder on 30 minutes contact time but after 60 minutes adsorption capacity of telescope snail shell powder tend to be higher than mangrove crab shell powder with increasing contact time. Telescope snail and mangrove crab shell adsorption capacity data at Table-1 were presented in graphical form that shown in Fig.-1, to know the adsorption capacity change for each adsorbents based contact time.

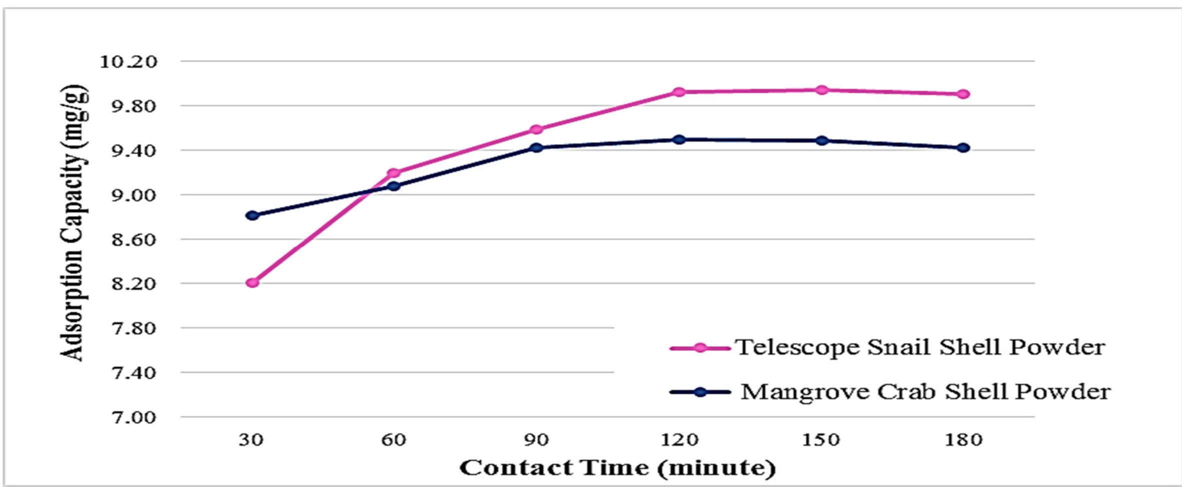

Fig.-1: Adsorption capacity based on contact time

Based on the graph shown in Fig.-1, at the contact time of 30 to 120 minutes of metal ions Pb^{2+} adsorption by both adsorbent showed improvement. It was indicated still not much that binds to metal ion Pb^{2+} so that it can perform effectively the entrapment. The longer contact time between the shell powder as adsorbent and the Pb^{2+} solutions as waste water synthetic, so more active side of the adsorbent which interacts with metal ions Pb^{2+} until 120 minutes and thereafter, no longer the adsorption of metal ions Pb^{2+} occurred. This condition indicated the active side of adsorbent has reached saturation point, where almost the entire surface has been covered by metal ions Pb^{2+}.

Adsorption equilibrium time occurs when the solution was contacted with the solid adsorbent and adsorbate molecules migrate from the liquid phase to the adsorbent, until not happen again adsorbate concentration changes, either in solution or in the adsorbent or adsorption speed with desorption have the same.[9] In this study, can conclude telescope snail shell and mangrove crab powder were reached adsorption equilibrium time on 120 minutes. Although both kind of adsorbent has the same adsorption equilibrium time, but when seen adsorption capacity value of them were different. On 120 minutes contact time, the adsorption capacity of telescope snail shell powder was 9.93 mg g^{-1} and for mangrove crab shell powder, was 9.50 mg g^{-1}.

Functional group and surface structure analysis

In this study, the functional groups of the adsorbent of telescope snail and mangrove crab shell powder determined based FTIR analysis, so it can be presumed mechanism of adsorption occured. In the analysis of FTIR spectra adsorbent conducted in this study, to be considered was the functional group shown presence of chitin and carbonate compounds. Both of these compounds are thought to play role in the adsorption of metal ions Pb^{2+}.

The compound chitin to note was the absorbance at some range of wavenumbers, among others: the wavenumber 1020 to 1200 cm^{-1} are the absorbance of the functional group bonding (C-N), 1650 to 1690 cm^{-1} are the absorbance of carbonyl functional group (C=O at $-HCOCH_3$), 2900 to 3350 cm^{-1} contained an amide bond functional group (N-H), and the wavenumber 3350 to 3500 cm^{-1} are the absorbance of the hydroxyl functional group (OH).[10,11,12] Meanwhile, to the carbonate compound to note was the absorbance at the wavenumber around 1400 to 1550 cm^{-1}, which was present in the range of carbonate groups (C=O asymmetric stretching of carbonate).[7] The results of the FTIR spectra analysis of telescope snail and mangrove crab shell powder after the adsorbent used for adsorption can be seen in Fig.-2 and Fig.-3.

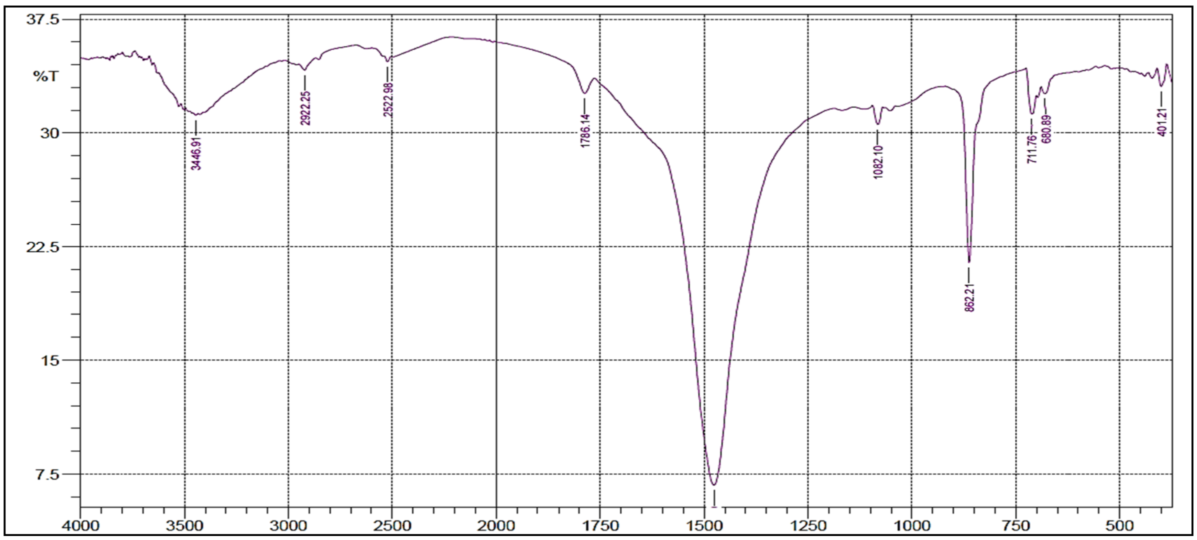

Fig.-2: FTIR spectrum of telescope snail shell powder

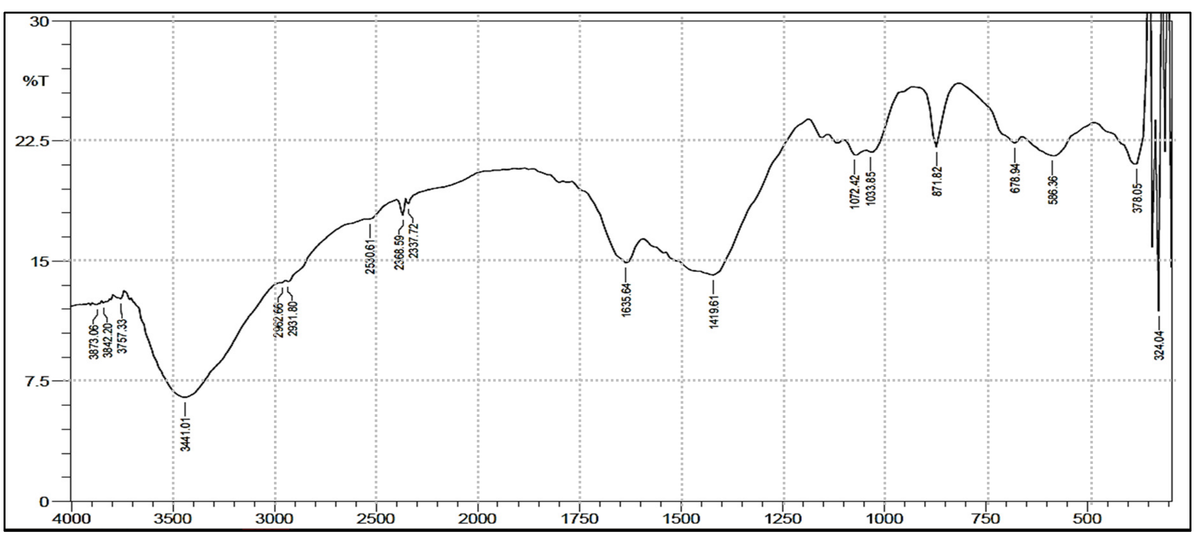

Fig.-3: FTIR spectrum of mangrove crab shell powder

The results of the analysis of functional groups of telescope snail and mangrove crab shell powder after use as adsorbent metal ions Pb^{2+} shown at Table-2.

Table 2. Result of functional groups of telescope snail and mangrove crab shell powder

Compound	Functional Group	Wavenumber (cm^{-1})	
		Telescope Snail (Telescopium sp) Shell Powder	Mangrove Crab (Scylla sp) Shell Powder
Chitin	C-N	1082.1	1033.85; 1072.42
	C=O (–$NHCOCH_3$)	-	1635.64
	N-H	-	2962.66
	O-H	3446.91	3441.01
Calsium carbonate	C=O (Carbonate)	1475.59	1419.61

Based on Table-2, showed that the telescope snail shell powder no visible bond of carbonyl (C=O at -$NHCOCH_3$) and amides (N-H), which was the typical functional groups on the compound chitin. Allegedly, this was due to the high mineral content in high telescope snail shell, thus masking the presence of compounds chitin. Meanwhile, the results of FTIR analysis of mangrove crab shell adsorbent powder showed a typical functional groups of chitin or carbonate compounds. Visibility of carbonyl (C=O at -$NHCOCH_3$) and amides (N-H) functional group in the FTIR spectra for both materials known to contain chitin was considerably higher than the telescope snail shell. Not only functional group typical compound chitin, but also seen the peak of the wavenumber carbonate functional group (C=O, asymmetric stretching of carbonate), which shows that it contains carbonate compounds in it.

Calcium carbonate has crystal structure of face-centered rhombohedral[13], where in the structure has a lot of empty space which allows charged by metal ions Pb^{2+}. Ions of Pb^{2+} not just occupy space. Pb^{2+} as divalent metal grating on the surface of calcium carbonate (calcite) in this state, cation adsorbed by Ca sites that form coordination bonds with CO_3. Metal ions Pb^{2+} bound as complex on the surface of the square-pyramidal. The formation of this complex was thought to occur in typical functional groups of chitin compounds with metal ions lead(II).[14] The formation of complex compounds characterized by numbers peak at wavelength 324.04 cm^{-1}. Wavelength regions used in the far infrared spectroscopy tool (400-10 cm^{-1}) was useful to know the molecules that contain heavy atoms. Results surface structure analysis of telescope snail shell powder after being used as adsorbent by the SEM analysis can be seen in Fig.-4.

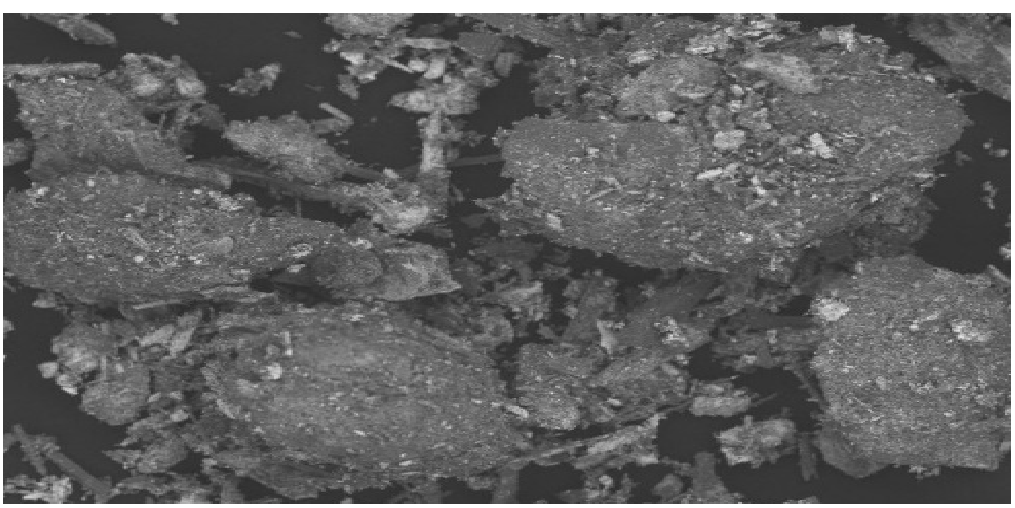

Fig.-4: Surface structure of telescope snail shell powder

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Meanwhile, the chemical composition of the telescope snail shell powder had used as adsorbent based EDX analysis can be seen in Table-3. EDX analysis results indicate the presence of the elements carbon, oxygen, calcium, and Pb^{2+}.

Table-3: Chemical composition of the telescope snail shell powder

Element	% mass
Carbon (C)	39.396
Oxygen (O)	37.141
Calcium (Ca)	12.395
Lead (Pb)	11.067

CONCLUSION

Telescope snail and mangrove crab shell powder in adsorb metal ion Pb^{2+} case reached adsorption equilibrium time on 120 minutes with adsorption capacity 9.93 mg g^{-1} for telescope snail shell powder and 9.50 mg g^{-1} for mangrove crab shell powder. The results of FTIR analysis showed that functional groups of telescope snail shell powder dominated by carbonates, while the functional groups of mangrove crab shell powder obtained typical compound of chitin and carbonate. Based on the results of this study, telescope snail and mangrove crab shell wastes can be used for the removal of Pb^{2+} from aqueous solutions.

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[RJC-1484/2016]