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Adsorption and Removal of Zinc (II) from Aqueous Solution Using Powdered Fish Bones

Han Khim Lim[a], Tjoon Tow Teng[a*], Mahamad Hakimi Ibrahim[a], Anees Ahmad[b] and Hui Teng Chee [a]

[a]*Environmental Technology Division, School of Industrial Technology, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia.*
[b]*Analytical and Environmental Chemistry Division, Department of Chemistry, Aligarh Muslim University, Aligarh, India.*

Abstract

The present work is an attempt to determine the feasibility and reliability of fish bones utilized as an adsorbent for the removal of zinc (II) from aqueous solution. The effects of solution pH, adsorbent dose and contact time on the adsorption process with respect to the zinc (II) removal were investigated via batch techniques at room temperature. The reaction kinetics of the zinc (II) removal from the aqueous solution were identified and correlated to the pseudo-first- and second-order kinetic models. The results obtained from the experimental work showed that fish bone can be transformed into adsorbent for removing metal ions from the aqueous solution. The results revealed that 98% of zinc (II) able to be sequestered under best adsorption conditions: pH 5.0, adsorbent dose = 1.80 g/100 mL, and 12 hours reaction time. The kinetic data was fitted to pseudo-first order and pseudo-second order, and was identified follow closely to pseudo-second-order kinetic model. Fish bones show promising results in removing zinc (II) from aqueous solution, thus this material could be used as low cost adsorbent to replace the expensive commercial activated carbon during adsorption process.

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Keywords: Adsorption; Fish bones; Zinc (II); Kinetic study.

1. Introduction

Over the years, the percolation of heavy metals into the water bodies and ecosystem remain as one of the most elusive and pervasive environmental threat to the global occupants. Heavy metal ions are classified as priority pollutants based on their toxicity and mobility in natural water streams. Nevertheless, the heavy metal ions are stable and persistent to environment changes since they cannot either be

* Corresponding author. Tel.:+6-04-653-2215; fax:+6-04-6573678.
E-mail address: ttteng@usm.my.

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degraded or destroyed [1]. The increment of industrialization has aggravated the situation due to the mass loading of highly concentrated metal ions containment effluent into the waterways.

To date, various treatment approaches have been applied by scientific community in order to decontaminate the water free from any heavy metal ions. These methods including adsorption, complexation, chemical oxidation or reduction, chemical precipitation, reverse osmosis, ion exchange, solvent extraction, membrane filtration, coagulation, phytoextraction and evaporation [2]. Adsorption is one of the most cost-effective methods due to its ease to operate, high efficiency and low maintenance cost whereas other treatment alternatives may have some disadvantages such as high consumption of reagent and energy, incomplete metal removal, low selectivity, high operational cost and problem in disposing the secondary waste generated during the treatment process [2]. Activated carbon has been the most respective and widely used adsorbent but it is relatively expensive in price. Therefore, this scenario has prompted the exploration of low cost adsorbent to be used as replacement for activated carbon.

The feasibility and reliability of lignocellulosic biomass, natural clay minerals and biological-based materials used as low cost adsorbent has been evaluated by many researchers. These materials including sugarcane bagasse, risk husk, tea leaves, bamboo dust, maize cob, tree sawdust [3], zeolite [4, 5], bentonite [6, 7], montmorillonite [8], *Cephalosporium aphidicola* [9], *Pinus sylvestris* [10], *Saccharomyces cerevisiae* [11], and so forth. Despite the mentioned materials, animal bones can also be utilized as adsorbents to remove heavy metals from aqueous solution. Bones are composed of 70% inorganic phase and 30 % organic compounds by weight. Calcium Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ [HAP], a main component in the inorganic phase exhibits its adsorptive behaviour via ion exchange reaction, surface complexation with phosphate, calcium and hydroxyl groups and/or co-precipitation of new partially soluble phases [12].

In this study, the effectiveness of fish bones used as adsorbent for the removal of Zinc (II) [Zn^{2+}] from aqueous solution was evaluated. The effects of pH, adsorbent dose, and contact time on the uptake of Zn^{2+} by fish bones were determined.

2. Materials and Methods

2.1. Preparation fish bones sorbents

Fish bones were collected from a local hawker stall in Bukit Mertajam, Penang, Malaysia. Then, the collected fish bones were washed several times with hot distilled water to remove the residue and soluble impurities from the bones. Next, the washed fish bones were dried in an oven at 80℃ and ground into fine powder.

2.2. Pretreatment of fish bones sorbents

The pretreatment method was obtained from the cleaning procedure described by Kizilkaya et al. [13]. The ground fish bones (solid-liquid ratio, 1:50, w/v) were stirred in 0.1 M NaOH aqueous solution at 60℃, 150 rpm shaking rate for 2 hours. Then, the treated fish bones were filtered, dried in an oven at 80℃ for 24 hours; milled and sieved in the size range of 125~250 μm. Finally, the treated fish bones powder was kept in an air tight container and ready to be used.

2.3. Preparation of stock of metal

All the chemicals procured and applied in this study were analytical grade. Stock solution of Zinc was prepared using $Zn(NO_3)_2.6H_2O$ in distilled water. Different desire concentrations of Zn^{2+} were prepared

by diluting 10000 mgL^{-1} of the stock solution. Standard solution of Zn^{2+} (1000 mgL^{-1}) for atomic absorption spectrophotometer was obtained from Merck.

2.4. Characterization of fish bones

The surface morphology and surface functional groups of the fish bones were analysed using Leo Supra 50 VP Field Emission Scanning Electron Microscope (Carl-Ziess SMT, Oberkochen, Germany) and Fourier Transform Infrared (Thermo Scientific FT-IR System Nicolet iS10 Model) with the spectra were recorded from 4000 to 400cm^{-1}.

2.5. Batch adsorption studies

Sorption capacity of fish bones was determined by contacting 1.0 g of fish bones with 100 mL Zn^{2+} solutions of known concentration (20-100 mgL^{-1}) in 250 mL Erlenmeyer flasks, shaken on a temperature-controlled shaker. The suspensions were agitated at 125 rpm, filtered out at the end of pre-determined time intervals, and finally analyzed for its metal ion concentrations using Atomic Absorption Spectrophotometric analysis (Analyst 200 AA, Perkin Elmer, USA). The rate of metal sorption by fish bones was determined by analysing the residual metal in the supernatant after contact durations of 5, 10, 15, 20, 25, 30, 60, 120, 240, 480 and 720 min. The effect of sorbate to sorbent ratio for the percentage and unit metal sorbate sorption capacity of the fish bones sorbent was determined by varying the solid mass phase between 1.0 g -1.8 g of fish bones. The effect of pH on the metal sorption by fish bones was evaluated in the range of 2.0-10.0. The initial pH of the metal solution was adjusted to the desired pH value using 0.1 M H_2SO_4 or 0.1 M NaOH. Numerous initial metal concentrations (20, 40, 60, 80, and 100 mgL^{-1}) were also been determined throughout the study. Fish bones-free and metal-free blanks were used as the experimental control. In order to avoid discrepancy experimental results, the experiments were performed in triplicate and the average values were used in data analysis. The percentage of metal adsorption by the adsorbents was calculated using this equation:

$$\text{Adsorption efficiency}(\%) = \left\{\frac{C_i - C_e}{C_i}\right\} \times 100 \quad (1)$$

where C_i and C_e are the initial and equilibrium concentration of metal ion (mgL^{-1}) in the solution. Adsorption capacity was computed by using the mass balance equation for the adsorbent:

$$\text{Adsorption capacity}(mg/g),\ q = \frac{(C_i - C_e)V}{W} \quad (2)$$

where C_i and C_e (mgL^{-1}) are the concentration of Zn^{2+} at initial and equilibrium time t, respectively, V is the volume of Zn^{2+} solution (L) and M is the mass of fish bones (g).

3. Results and Discussion

3.1. SEM and FTIR of fish bones

Fig. 1 shows the SEM micrographs of the fish bones prior to the adsorption process. It is noticed that fish bones have several numbers of heterogeneous porous layer which may provide a good possibility of Zn^{2+} to be adsorbed on its surface. Next, the clear openings of the pores also ease the accessibility of metal ions into the internal part of the bones.

The FTIR spectrum for the surface functional groups of fish bones is presented in Fig. 2. The spectrum shows distinct peaks at 3423. 98 (N-H stretch), 2922.50 (C-H stretch), 2851.83 (C-H stretch), 2359.82 (N-H stretch), 1663.32 (C=O stretch), 1551.65 (N-H stretch), 1458.02 (N=O stretches), 1027.56 (C-O-C stretch), and 872.57 (C-C stretch).

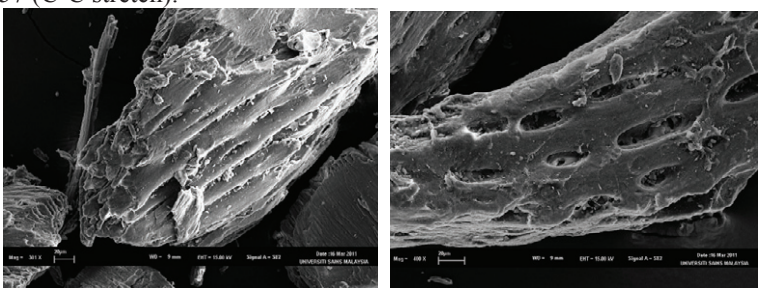

Fig. 1. SEM image of fish bone.

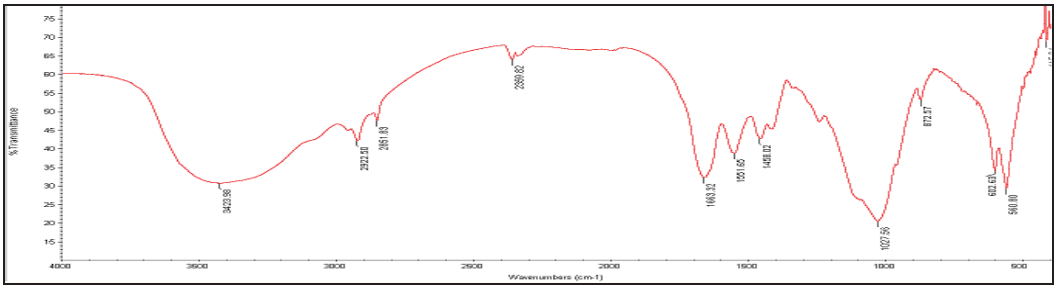

Fig. 2. FTIR spectra of fish bone.

3.2. Effect of solution pH on Zn^{2+} adsorption

The effect of solution pH on the Zn^{2+} removal was studied by varying the initial pH of the Zn^{2+} solution and keeping the other process parameter constant. The experiments were carried out at 1.0 g/100 mL fish bones mass at room temperature for 30 min equilibrium time at different initial pH of dye solution (pH 2.0 ~ pH 10.0). The effect of solution pH on the uptake of Zn^{2+} is presented in Fig. 3. The data indicates that Zn^{2+} removal favourable with the addition of fish bone used as adsorbent as compared to the solution solely pH adjusted. The figure also shows that Zn^{2+} removal increased drastically in pH from 6 to 10. At low pH, low metal adsorption has been caused by the competition of metal ions with hydrogen ions for the available adsorption sites as well as the positive charge density on the metal binding sites where high concentration of protons in solution inhibiting metal removal. In contrast, the negative charge density on the adsorbent surface increases as pH increases due to deprotonation of metal binding sites and thus enhance the adsorption efficiency [14]. Experiments were carried out at pH 5 due to Zn^{2+} obtained best removal at this pH value in acidic range plus metal precipitation occurred at higher pH values.

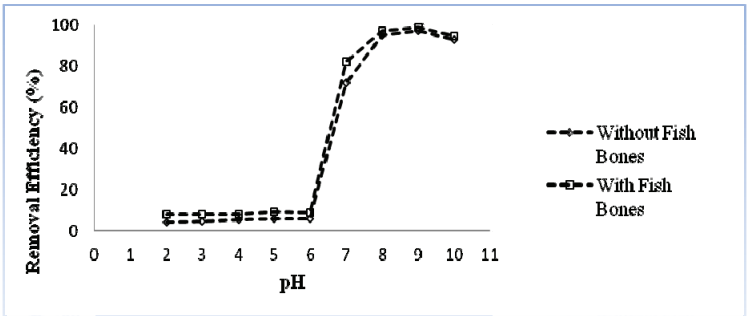

Fig. 3. Effect of solution pH on equilibrium uptake of Zn^{2+} with and without addition of fish bones.

3.3. Effect of adsorbent dose and contact time on Zn^{2+} uptake

The effect of adsorbent dose on the amount of Zn^{2+} adsorbed at a series of contact time experiments is illustrated in Fig. 4. The maximum adsorption capacity of Zn^{2+} onto the fish bones adsorbent was observed at 12 h using 1.8 g/100 mL fish bones adsorbent which potential to remove 98.0 % Zn^{2+} from aqueous solution. The data shows that increasing the adsorbent dose will enhance the adsorption of Zn^{2+} since the number of metal binding sites increase as well. Longer contact time provides sufficient duration for the adsorption process to take place and thus enhance the metal ions uptake from the solution onto the metal binding sites of the adsorbent.

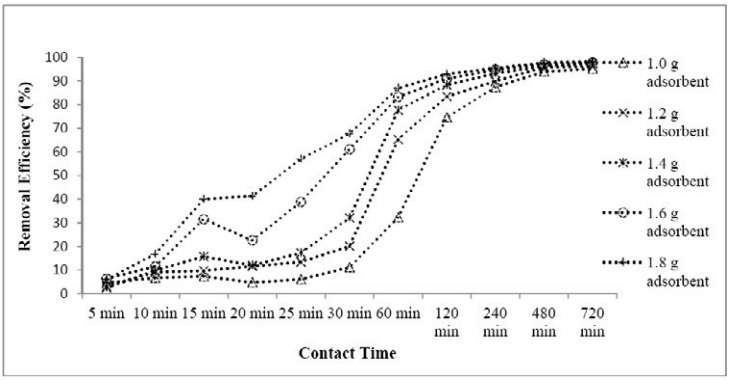

Fig. 4: Effect of fish bones adsorbent dose on the removal of Zn^{2+} at different reaction time (pH5.0, room temperature 30 ±1 ℃).

3.4. Adsorption Kinetics

Pseudo-first-order and pseudo-second-order kinetic models were introduced to the experimental data in order to investigate the adsorption kinetics of Zn^{2+} onto the fish bone adsorbent.

Pseudo-first-order was reported by Lagergren and Svenska [15]. The pseudo-first-order equation can be written as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (3)$$

Integrating Equation 3 for the boundary conditions t=0 to t=t and q_t=0 to q_t=q_t, results

$$\ln(1-\frac{q_t}{q_e}) = -k_1 t \quad (4)$$

where k_1 is the rate constant (h^{-1}), q_e (mg/g) is the amount of solute absorbed onto the activated carbon surface at equilibrium, q_t (mg/g) is the amount of solute adsorbed at any time t, and is provided by Equation 5.

$$q_t = \frac{(C_o - C_t)V}{M} \quad (5)$$

Pseudo-second-order equation can be written as:

$$\frac{1}{q_t} - \frac{1}{q_e} = \frac{1}{k_2 q_{e^2} t} \quad (6)$$

where k_2 (g/mg.h) is the pseudo-second-order rate constant. Both k_1 and k_2 values can be calculated from the slopes of the plots $\ln\left(1-\frac{q_t}{q_e}\right)$ versus t and $\frac{1}{q_t}-\frac{1}{q_e}$ versus $\frac{1}{t}$, respectively.

Information about the pseudo-first- and pseudo-second order models are summarized in Table 1 which presents the comparison of adsorption kinetics data for both models with different initial Zn^{2+} concentrations at different times. The correlation coefficient values for pseudo-first-order kinetic model obtained were relatively small whereas the experimental q_e values did not fulfil the calculated values gained from the linear plots that illustrated in Table 1. Therefore, adsorption Zn^{2+} onto the fish bones adsorbent of did not follow pseudo-first-order model.

Table 1. Comparison of the pseudo-first- and second-order adsorption rate constants, calculated and experimental q_e values for different initial Zn^{2+} concentrations.

*C*o	First-order kinetic model				Second-order kinetic model		
(mgL-1)	qe,exp (mg/g)	qe,cal (mg/g)	*k*1	*R*2	qe,cal (mg/g)	*k*1	*R*2
20	1.92	1.80	0.333	0.49	1.93	0.014	0.96
40	3.90	3.64	0.327	0.54	3.92	0.004	0.79
60	5.89	5.86	0.572	0.43	5.92	0.002	0.65
80	7.89	7.62	0.411	0.78	7.90	0.002	0.96
100	9.90	9.61	0.438	0.63	9.89	0.001	0.88

Next, the correlation coefficient values for pseudo-second-order show higher results as compared to the values of pseudo-first-order (presented in Table 1). The experimental and calculated q_e values are very close, indicating the applicability of pseudo-second-order in order to describe the reaction of Zn^{2+} adsorbed onto the fish bones adsorbent.

4. Conclusion

This work revealed the fact that fish bones can be a promising material to be transformed into adsorbent for removing Zn^{2+} from aqueous solution. Under best adsorption conditions pH 5.0, adsorbent dose 1.80 g/100 mL solution, and 8 h reaction time at room temperature 30 ±1°C, 98% of Zn^{2+} had been removed from aqueous solution. The reaction kinetic of Zn^{2+} adsorbed onto the surface of fish bones was

found follow closely to the pseudo-second-order model. Removal of Zn^{2+} from aqueous solution via adsorption process was identified to be dependent on solution pH, adsorbent dose as well as contact time.

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