

## BIOSORPTION OF Zn(II) IN HIGH AND LOW STRENGTH SYNTHETIC WASTEWATER BY WATERMELON RIND (*CITRULLUS LANATUS*)

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**Abstract.** The heavy metal contain in the industrial wastewater can cause a pollution towards the environment and human due to its toxicity. Therefore extensive studies were conducted for the heavy metal removal. This study was conducted under several conditions by varying pH, biosorbent dosage, initial wastewater concentration and contact time. The results revealed that optimum pH, for high strength synthetic wastewater was 8.0 meanwhile for low strength synthetic wastewater was 7.0. Both high and low strength synthetic wastewater was optimum at 30 minutes of contact time with 1.5g and 0.02g of bisorbent dosage respectively. Meanwhile, the optimum initial metal concentration for high and low strength synthetic wastewater was 400ppm and 1ppm respectively. The results had proven that watermelon rind is able to treat wastewater with high and low concentration of metal.

### Introduction

The contamination of heavy metals due to industrial activities can lead to the pollution in surface, ground or sea water. Industries from mining, metal plating, painting, tanneries, battery manufacturing and metal finishing usually discharge heavy metals as toxic substances [1]. Therefore it is important to treat the heavy metals from the industrial wastewater.

Heavy metals are non-biodegradable material which can increase the toxicity that accumulates through the biomagnifications and food chain. The increasing toxicity, thus can give a bad impact to the ecosystem and human health [1]. The heavy metal ions that normally discharge by copper, cadmium, lead, nickel, and chromium [2].

Therefore, various techniques have been explores for the treatment of metal-bearing industrial wastewater including chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction. However, all these methods can extremely expensive or inefficient, often resulting problems of low selectivity, incomplete removal and producing large quantities of waste [1,3,4].

As a consequence, the finding for a new effective technology has directed attention to the biosorption process has using biological material as sorbent [5]. Compared with conventional method, the biosorption process offers the advantages of low operation cost, minimization of the volume of chemical and/or biological sludge to be disposed of, high efficiency in detoxifying very dilute effluents, and no nutrient requirements [6]. Therefore this research will study about unexploited fruit waste namely, watermelon (*Citrullus Lanatus*) as a new biosorbent material for zinc metal treatment from industrial wastewater

## Material and methods

**Biosorbent preparation.** The watermelon rind was collected from the local fruit stalls at Batu Pahat, Johor, Malaysia. The rinds were washed with distilled water for several times and soaked into Nitric Acid ( $\text{HNO}_3$ ) for about 24 hours to remove all the dirt particle and/or unwanted contaminants present on the surface of watermelon rind and further cleaned with deionized water. Then the biosorbent was oven-dried at  $60^\circ\text{C}$  until constant weight. The dried rinds were grounded using laboratory ball mill to produce particle size passing sieve  $150\ \mu\text{m}$  and preserved in polythylene container for further use as biosorbent [3].

**Batch Studies.** A stock solution of zinc ( $1000\text{mg/l}$ ) was prepared in deionized water by using zinc sulfate ( $\text{ZnSO}_4(\text{H}_2\text{O})_7$ ). The others varying working range concentration solution were getting from successive dilution. The pH required value for the solutions was adjusted by adding a few drop of diluted  $0.01\text{M}$  HCl or  $0.01\text{M}$  NaOH using PH meter. All samples were shaken at  $125\ \text{rpm}$  at room temperature. Then the solutions were filtered using  $0.45\ \mu\text{m}$  membrane cellulose filter. The concentrations of heavy metals contained in wastewater were analyzed by using Atomic Absorption Spectrometry (AAS). The biosorbent were analyzed by using Scanning Electron Microscope (SEM), X-ray Fluorescence Analysis (XRF).

## Result and discussion

**XRF analysis.** The present of  $\text{SiO}_2$  ( $83.70\%$ ) and  $\text{CaO}$  ( $2.18\%$ ) in the watermelon rind elements show that the watermelon rind is a good sorbent material [3].

**SEM analysis.** The surface morphology, structure of the biosorbent and elemental analysis were determined by using Scanning electron microscopy [3,7]. Biosorbent before biosorption process were observed (refer with: Fig1 Micrograph of biosorbent). The SEM result indicate that the watermelon rind rough surface texture and porosity could be distinctly noticed, making it is possible for the various heavy metals to be adsorb by different parts of the biosorbent. Figure (ref with : Fig 1) also shows there have two types of colours which are white and dark region in the watermelon rind. The white area contains an inorganic element of silica, meanwhile the dark area comprises of organic protein which are rich in carbon and oxygen [7].

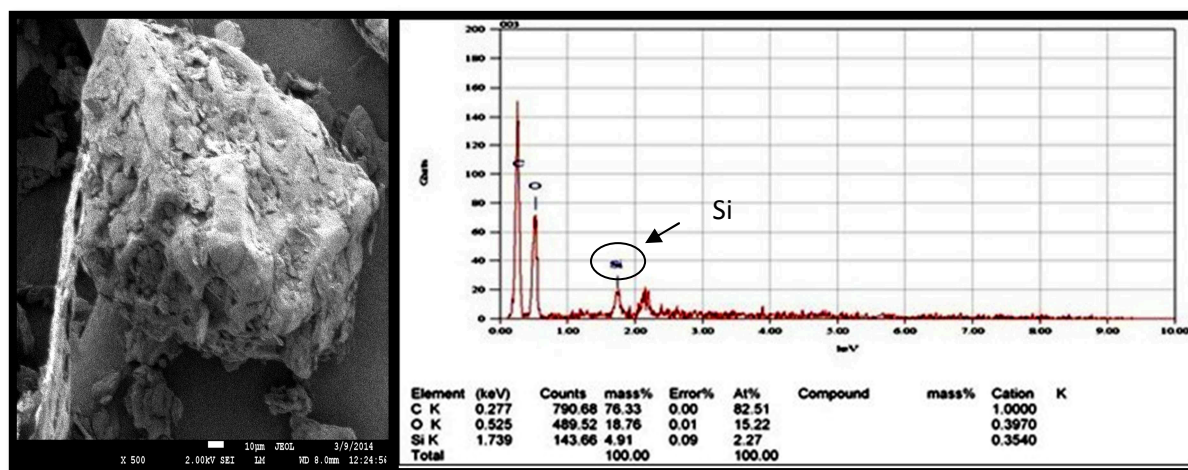


Figure 1: SEM micrograph of biosorbent

**Effects of pH on biosorption.** The biosorbent capacity of heavy metals can be affected by the parameters of pH. The biosorption of zinc towards the influence of hydrogen ion concentration were studied by varying the pH of zinc solution [8]. In this study, the effect of pH was studied in the range 6.0 to 9.0 for high strength wastewater and 6.0 to 7.5 for low strength wastewater. Table (ref with: Table1, Table2), show the maximum uptake of zinc for high and low strength synthetic wastewater was 31.29 mg/g at pH 8 and 17.29 mg/g at pH 7.0 respectively. The competition of large quantities of proton and metal ion for active site surface cause by the low pH can effect the biosorption uptake capacity either in high strength or low strength wastewater [7]. Table (ref with: Table1, Table2), also give a significant result where the increasing of pH solution from pH 7.0 for low strength wastewater to pH 8.0 for high strength wastewater effect the biosorption uptake capacity when the competition of proton and metal ions became passive. Meanwhile the optimum percentage removal for high strength wastewater was 78.23% and the optimum percentage removal for low strength wastewater was 34.50%.

**Effects of biosorbent dosage on biosorption.** The effective metal removal can be determine by considering the biosorbent dose as a significant factor. The sorbent-sorbate equilibrium of the system also can be determine by biosorbent dose [8]. The effective biosorbent amount was found to be 1.5g for high strength wastewater and 0.02g for low strength wastewater with the removal of 83.33% and 54.0% of zinc in the synthetic wastewater. The percentage removal of zinc metal ions will increased due to the increasing of biosorbent amount untill the saturation point [3]. However the increasing of biosorbent amount will decreased the biosorbent uptake capacity. About 22.22 mg/g of uptake capacity was recorded for high strength synthetic wastewater and 27.30 mg/g for low strength synthetic wastewater.

**Effects of initial metal concentration on biosorption.** Initial metal ions concentration was the factor influent the biosorption of metals. The results indicate that the increasing of initial metal ion concentration will increased the biosorption capacity [8]. It shows in table (ref with: Table 1) where the optimum percentage removal of zinc was 82.83% with the 22.09 mg/g uptake capacity at concentration 400ppm, meanwhile table (ref with: Table 2) shows the optimum percentage removal of zinc at low strength synthetic wastewater was decreasing to 79.90% at concentration of 1ppm with 39.95 mg/g of uptake capacity. High solute uptake results from the higher initial concentration because the sites available for sorption become lesser in higher concentration. Therefore it is necessary to determine the optimum saturation potential of biosorbent because the studied should be tested at the maximum possible initial solute concentration [1].

**Effects of contact time on biosorption.** The highest percentage removal efficiencies will determine the optimum contact time. It has been observed that maximum removal for high and low strength synthetics wastewater took place within 30 minute of contact time with 83.40% and 80.67% removal respectively. Where at this point, the amount of absorb from the biosorbent was in a state of dynamic equilibrium with the amount of metals being absorbed onto the biosorbent. The equilibrium time and the amount of metals absorbed at this equilibrium time reflected the optimum metals biosorption capacity of the biosorbent under the certain condition [9]. Hence the uptake capacity for high strength synthetic wastewater was 22.20 mg/g and for low strength synthetic wastewater was 40.35 mg/g.

*Table 1: Result for high strength synthetic wastewater*

Parameter	Optimum		Uptake capacity, Qeq, mg/g
	Parameter	Percentage removal, %	
pH	8	78.23	31.29
Biosorbent amount [g]	1.5	83.33	22.22
Zinc concentration [mg/l]	400	82.83	22.09
Contact time [minute]	30	83.40	22.20

Table 2: Result for low strength synthetic wastewater

Parameter	Optimum		Uptake capacity, Qeq, mg/g
	Parameter	Percentage removal, %	
pH	7	34.50	17.25
Biosorbent amount [g]	0.02	54.00	27.30
Zinc concentration [mg/l]	1	79.90	39.95
Contact time [minute]	30	80.67	40.35

### Comparison between high strength and low strength synthetic wastewater

The pH usually important role among the others various factors in the biosorption process, which can affect the solution chemistry of metals and the activity of the functional groups of the biosorbent and can even completely alternate the activity binding sites [7]. The increasing of pH will increase the percentage removal efficiency [9]. Table (ref with: Table 1, Table 2) show that the high strength synthetic wastewater give a higher percentage removal then the low strength synthetic wastewater due to the increasing of pH. The same trend of results was found for others parameters namely biosorbent amount, concentration and contact time. The biosorbent amount added to the solution determines the number of binding sites available for absorption [9]. The biosorbent amount for the high strength synthetic wastewater consume a higher percentage removal compare to the low strength synthetic wastewater, but the uptake capacity was decreased due to the overlapping or aggregation of adsorption sites resulting in a decreased in total adsorbent surface area [8]. In general the results in table (ref with: Table 1, Table 2) indicate, that optimum percentage removal of high strength synthetic wastewater is higher compare to low strength synthetic wastewater. This is proven by the percentage removal of high strength is high as 82.83% compare with low strength wastewater only 79.90%. Meanwhile for both synthetic wastewaters the optimum contact time were achieve at 30 minutes of contact time with the percentage removal more than 50% for both strengths.

### Conclusion

The watermelon rind (*Citrullus Lanatus*) can be used as a biosorbent to remove metal of zinc in high and low strength wastewater with 90% of percentage removal. It is a promising adsorbent in removing zinc in both high and low strength synthetic wastewater. Optimum condition of high and low strength synthetic wastewater are adjustment in term of pH, biosorbent amount, concentration and contact time.

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