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# Effect of pH on the biosorption of heavy metal by alginate immobilized durian (*Durio zibethinus*) seed

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## ABSTRACT

*The heavy metals biosorption by alginate immobilized durian seed biomaterial has been done in dry, gel bead and non-immobilized. Immobilization of durian seed powder into alginate was able to improve the performance of the biomass in adsorption process, increasing the uptake capacity, facilitate the separation of the biomass from the solution, can be regenerated without damaging the structure of the biomass and used repeated bio-sorbent. In this study specifically studied the effect of pH on the uptake capacity of metals such as Pb(II), Cu(II), Cd(II) and Zn(II) on durian seed non immobilized and alginate immobilized biosorbent. pH was obtained for each metal ions was at pH 4-5 for Pb(II), pH 5-6 for Cu(II) and Cd(II), pH 4-5 for Zn(II) in alginate immobilized(dry and gel bead), non-immobilized and Ca-alginate matrix respectevely. The order of the uptake capacity was: alginate immobilized dry bead>non immobilized> gel bead> Ca-alginate.*

**Key words**: Biosorption, heavy metal, immobilization, alginate and durian (*Durio zibethinus*) seed.

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## INTRODUCTION

Heavy metal contamination of water has become one of the most serious environmental problems today [1].The heavy metals are non-degradable in the environmental and can be harmful to some living species. Beside the toxic and harmful effect to organisms living in water, they are also accumulate throughout the food chain and may effect of human health [2-3].

The contamination heavy metals such as lead, cadmium, copper, and zinc can from industrial activities such as mining, pigments, batteries, paints, ammunition, petrol, cable, alloys and steel, plastics, industrial glass, electroplating, electrolysis, photography, burning coal, industrial printers and the like [2,4-6].

The conventional removal methods for heavy metals from water and wastewater such as chemical precipitation, solvent extraction, reverse osmosis, filtration, ion exchange, coagulation electro-dialyses electro-flotation, adsorption and biosorption [7]. Among these methods, biosorption is attractive methods which involved sorption of dissolved substances by biomaterial. The main advantage of this technique can be ordered: low operating cost, improved selectivity and reusability of biomaterial, short operation time and no production of secondary compounds [8].

The bio-sorbents can from agriculture waste or forestry by product such as rice husk [9], *ocimum bacilicum* seeds[10], sour-sop seed (*Annona muricata*) [11], saw dust [12]. The biosorption of heavy metals by these materials might be attributed to their carbohydrates, proteins, and phenol compounds having carboxyl, hydroxyl, sulfate, phosphate and amino groups [13].

Durian (*Durio zibethinus*) consists of cellulose (60.5 %), holocellulose (73.5%) and hemicellulose (13.1%)[14], these characteristics make durian seed can be used heavy metals bio-sorbent. Research on alginate immobilized durian seed as heavy metals bio-sorbent no reported by other researchers. Preliminary research has been studied biosorption of Zn(II) using durian seed bio-sorbent [15]. Durian seed powder have disadvantaged in the water, where it have polysaccharide gums are highly hydrophilic substance that are soluble or dispersible in water [16]. It can granulation in aqueous solution and difficulties to separate from aqueous solution.

In industrial operation, immobilization is one of the methods used to overcome the incorporating free suspended biomass in wastewater treatment. It offers several advantages include minimal clogging in continuous system and can be regenerated [17]. The bio-sorbent are easy to separate from the reaction system and can be regenerated [18]. Biopolymer such as alginate are widely used as immobilization matrices as they are non-toxic and efficient [19].

The present study was conducted to determine the ability of immobilization biomass of durian seed in alginate (gel and dry bead) and non-immobilized. The objective of the present work was investigated the effect of pH on the biosorption heavy metals by alginate immobilized durian seed bio sorbent.

## MATERIALS AND METHODS

### Reagents

All analytical grade chemical reagents including $Pb(NO_3)_2$, $Cd(NO_3)_2$, $Cu(SO_4)_2$, $Zn(SO_4)_2$, HCl, $HNO_3$, $CH_3COOH$, NaOH, $NH_4OH$, sodium alginate, $CaCl_2$ etc., used in these studies were purchase from Merck Germany.

### Preparation of Bio-sorbent

Durian seed samples collected from local market in Padang West Sumatra, Indonesia. Before use, they were washed with water several times to remove surface impurities. Samples were cut into thin slices with a size of 1-2 cm and then sample was dried at room temperature and then dried in oven at 60°C for 24 hours. The dried durian seed were ground using a grinding mill and then milled in the sieve with a particle size of 72 um and stored in glass containers until use for biosorption experiments.

### Pretreatment Biomaterial With Acids and Alkali.

Durian seed powder 10 g was soaked in a solution of $HNO_3$ 0.1 M, 0.1 M NaOH, 0.1 M HCl, $CH_3COOH$ 0.1 M with a ratio of 1: 10 and then shaker for 2 hours at 100 rpm. After that filtered and washed with distilled water until pH of about 6-7. Durian seed treated was dried in an oven at $60^oC$ for 24 hours and crushed to get particle size of 72 um.

### Bio-sorbent immobilization.

The employed cross-linking procedure with calcium alginate was an adapted version of the method of Reference [20].For alginate immobilized durian seed 2% polymer alginate solution is prepared by dissolved 2g of Na-alginate in 100 mL of deionized and subsequent agitation for 4-6 hours with a magnetic stirrer at 100 rpm and polymer suspension with 2g durian seed powder. The mixture was introduced into a solution containing 0.2 M $CaCl_2$ with a syringe and the solution was stirred to prevent aggregation of the durian seed entrapped in Ca-alginate bead. Beads (2-3 mm) were hardened in 2% $CaCl_2$ solution for 24 hours. Furthermore, beads were washed with distilled water while stirred with a speed of 100 rpm for 30 minutes and 3-5 times repeated until neutral pH. Beads divided into two form dry and gel beads. Dry beads were dried at room temperature and stored in a desiccator and gel beads were stored in distilled water at 4°C.

### Metal ions uptake studies.

Biosorption of Pb(II), Cd (II), Cu(II) and Zn(II) ions on plain Ca-alginate beads, free and alginate immobilized durian seed were carried out in batch system. The effect of pH on the biosorption rate was investigated in the pH range 2.0-7.0 (which was adjusted with $HNO_3$ or NaOH at the beginning of the experiment) at $27^oC$. Solution 20 mL containing 10 mg/L of each Pb(II), Cd(II), Cu(II) and Zn(II) ions and bio-sorbent were stirred at 150 rpm. After adsorption periods (60 min for non-immobilized) and (120 min for immobilized), the aqueous phases were separated from the adsorbent and the residual concentrations of the metal in these phases were measured by using flame Atomic Absorption Spectroscopy.

The uptake of metal ions was calculated from a metal mass balance using a following equations:

$$Qe = \frac{(Co - Ce)}{m} .V............(1)$$

Where: Qe is (mg) metal ion per (g) dry bio-sorbent. Co and Ce are the initial and residual metal concentration (mg/L)respectively, V is Volume (L) of metal ions, mis bio-sorbent mass (g).

## RESULTS AND DISCUSSION

### 3.1. Effect of Chemical Pretreatment.

Effect of the chemical pretreatmenton the uptake capacity can be seen in Figure 1.

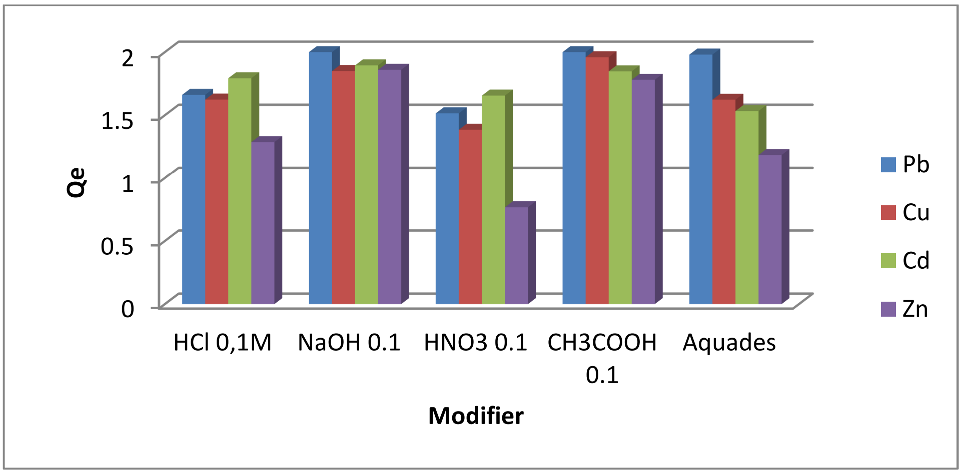


**Figure1: Effect of treatment durian seed powder on biosorption of Pb(II), Cu(II), Cd(II) and Zn(II) ions (pH of metals ion was 5, contact timewas60min, agitation speed was 150rpm, mass of bio-sorbent 0.1gand concentration of solution was 10mg/L)**

Treated durian seed powder with mineral acids, HCl and $HNO_3$can the uptake capacity is decreased without acidified, that was caused immersion using strong acids occur gelatinization, gel formation due to powder slightly soluble in strong acid or a process of hydrolysis. Durian seed polysaccharide contains which most polysaccharides are pectin and gum compounds. The pectin in strong acid solution can be extracted and release of the powder into a solution it will break the chain of polysaccharides, which can damage the surface structure and reduced site active on the surface bio-sorbent. The presence of gel in the solution will be difficulties to separated, filtrate will slow down due to high viscosity of the solution. Treated acid strong bio-sorbent when contacted with metals ion indicated that the uptake capacity of the metal ion decreased. Durian seed was treated with NaOH solution, the uptake capacity of the metal ions increased. This could be due to with NaOH solution non-gelatinization, it will be able to open surface pores bio-sorbent and site active group would negatively charge, so it will be able to increase uptake capacity metals ion. Removal Cu(II) by Rubber leaf (*Hevea brasilinesis*) biomass treated with NaOH reported [21].

Treated bio-material with acetic acid non-hydrolysis carboxyl site active groups on the surface of biomaterial. In acetic acid ($CH_3COOH$) contain hydroxyl groups, in the presence it will be able to added existing functional groups on the biomaterial surface, the uptake capacity to be increased. Biosorption of Pb(II) using original orange peel and protonated $HNO_3$, adsorption capacity 2 mmol/g (40% dry weight) at a concentration of 300 ppm reported [22] and peanut shell modified with formaldehyde and pyridine to the adsorption of Pb, Cd, Cu, Zn and Hg with the uptake capacity obtained was 5.01; 3.63; 2.18; 1.82 and 1.58 mg/g respectively while the modified pyridine obtained was 2.64; 3.63; 2.48, 6.92; 1.91 respectively for Pb, Cd, Zn, Hg and Cu [23].

Entrapment biomaterial durian seed into Ca-alginate bead order to obtained alginate immobilized bio-sorbent that have mechanical properties strong, resistant in acidic solutions, easy to separated, minimize clogging, improved the uptake capacity and can be regenerated. Diameter of beads 2-3 mm gel and 1 mm dry bead. Alginate immobilized durian seed bio-sorbent is depicted in Figure 2.


**Figure2: Non immobilized (A), gel(B) and drybead(C) bio-sorbent.**

### 3. 2. Effect of pH
### 3.2.1. Non Immobilized Bio-sorbent
The initial pH of the solution is a very important parameter for studying the process of metal biosorption [24]. This is related to the capability of the hydrogen ion competition with the active site on the surface bio-sorbent [25]. Effect of pH on the biosorption of metals ion Pb(II), Cu(II), Cd(II) and Zn(II) on non-immobilized bio-sorbent results are shown in Fig 4.

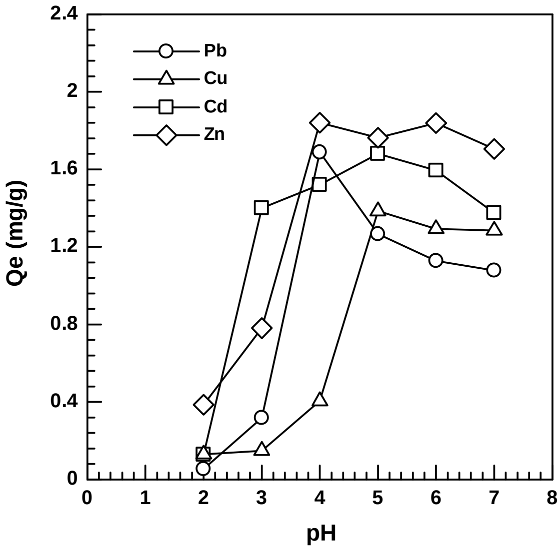


**Figure 4: Effect of pH on the uptake capacity of Pb(II), Cu(II), Cd(II) and Zn(II) on non- immobilized. (initial concentration 10 mg/L, particle size is 72 um, bio-sorbent mass is 0.1 g, contact time is 60 min, stirring speed is 150 rpm)**

The pH of ion Pb(II), Cu(II), Cd(II) and Zn(II) were studied from 2-7. From Figure 4 shows that the biosorption at low pH (2-3) gives lower uptake capacity, it was because of competition hydrogen ion with metals ion at the active sites [26].Surface of bio-sorbent was more negatively charged as the pH of solution increased 3 to 6. The functional groups of the biomass were more deprotonated and thus available for the metals ion [1]. Effect of pH on the uptake capacity of Pb(II), Cu(II), Cd(II), Zn(II) on non-immobilized obtained optimum at pH 4-5 with uptake capacity 1.688 mg/g, 1.385 mg/g, 1.681 mg/g and 1,84 mg/g respectively. Studied biosorption of Pb(II) ion on the shell and seeds of litchi, obtained pH 5 on seed and pH 3 on shell with the uptake capacity of 0.9691 mg/g and 0.7560 mg/g respectively [11]. Biosorption of Cu(II) on sunflower hulls and occurred pH at 5 [27]. Biosorption of Cu(II) used seed *Ocimum bacilicum* at pH 5 with uptake capacities was 60.5 mg/g [28].

### 3.2.2. Alginate immobilized durian seed(gel and dry beads).
Effect of pH on alginate immobilized durian seed bio-sorbent were studied in a gel, dry beads and Ca-alginate as a control at pH 2-7 for initial metal concentration of 10 mg/L. Effect of pH on uptake capacity bio-sorbent result are shown in Fig 5-7.

The uptake capacity was decreased at acidic pH (2-3) for Cu(II) ions and increased at pH 4-6. Cu (II) ions, optimum pH obtained at pH 5 for dry bead with the uptake capacity of 1,729, Ca-alginate between pH 5-6 with uptake capacity 0.985 mg/g and the gel bead was pH 6 with the uptake capacity 1.413 mg/g.

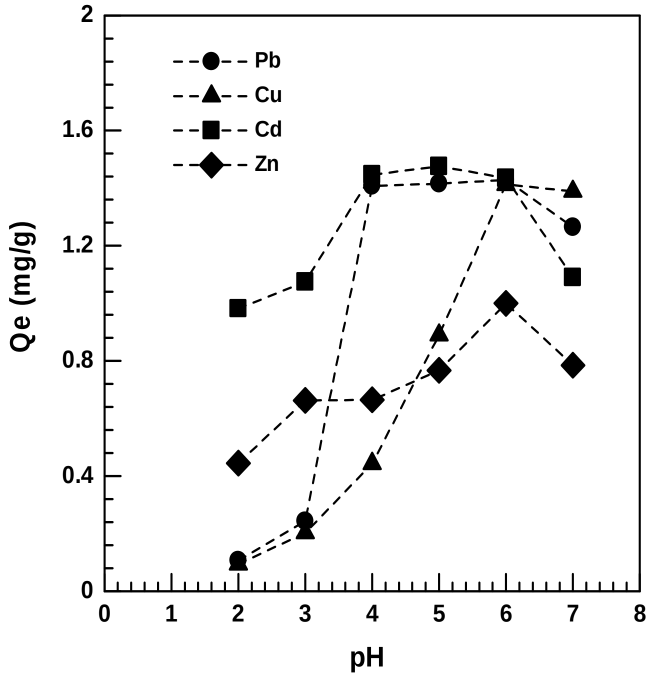


**Figure5: Effect of Ph onthe uptake capacity of Pb(II), Cu(II), Cd(II) and Zn(II) on alginateimmobilization durian seed (gel bead). (Initialconcentration:10mg/L; volume of solution: 20 mL; mass of bio-sorbent: 0.1g; agitation: 120 minutes; stirring speed: 150rpm)**

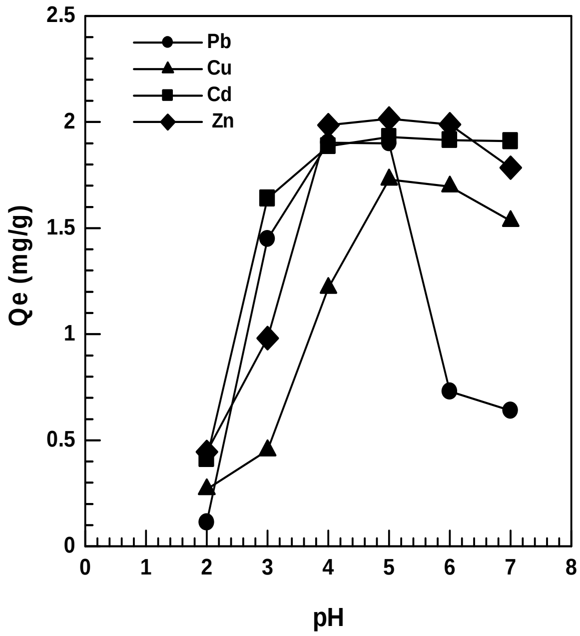


**Figure 6: Effect of pH on the uptake capacity of Pb(II), Cu(II), Cd(II) and Zn(II) on alginateimmobilization durian seed (dry bead). (Initial concentration:10mg/L; volume of solution: 20 mL; mass of bio sorbent: 0.1g; agitation:120 minutes; stirring speed: 150rpm)**

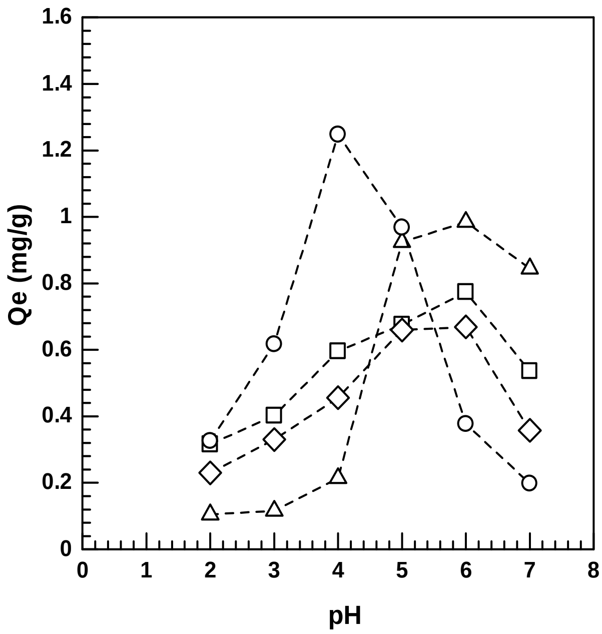


**Figure7: Effect of pH on the uptake capacity of Pb(II), Cu(II), Cd(II) and Zn(II) on Ca-alginate bio-sorbent. (Initial concentration :10mg/L; volume of solution : 20 mL; mass of bio-sorbent : 0.1g; agitation: 120 minutes; stirring speed: 150rpm)**

The uptake capacity of Pb(II), Cu(II), Cd(II) and Zn(II) ondry bead bio-sorbent increased than the gel bead and Ca-alginate due to alginate immobilization durian seed will work together to biosorption of heavy metals in solution. Ca-alginate has sufficient ability to biosorption metals ion because the presence of carboxylic groups on the surface of bio-sorbent. Carboxylic groups, this would be carboxylate ion at a pH of 5-6 where surface of bio sorbent will be negatively charged. Site active surface alginate immobilization will also negatively charge with increasing pH. While solution pH above 6, the $Cu^{2+}$ ions precipitate and making the biosorption impossible [17]. The optimum pH obtained for each metal ion Pb(II), Cu(II), Cd(II) and Zn(II) at pH 4-5 for dry bead, gel bead and Ca-alginate.The Uptake capacity Cd(II) by alginate immobilization (dry bead) 1.930 mg/g at pH 5, gel bead 1.476 mg/g at pH 5 and Ca-alginate 0.774 mg/g at pH 6.

The uptake capacity of Zn(II) on dry bead from 1.985 to 2.016 mg g at pH 4-5, gel bead 1.0 mg/g at pH 6 and Ca-alginate 0.66-0.669 mg/g at pH 5-6.The order effect of pH on uptake capacity metals ion Pb(II), Cu(II), Cd(II) and Zn(II) obtained were dry bead> non immobilized>gel bead>Ca-alginate. The capability biosorption alginate immobilization dry bead larger than non-immobilized and Ca-alginate due to the synergistic effect of alginate with carboxyl group and durian seed have carboxyl and hydroxyl groups. Several studies reported that immobilization generally increase metal accumulation by biomass. Biosorption of Cu(II) using *Penicillium citrinum* free and immobilized alginate have been studied. Optimal pH adsorption obtained at pH 5 with uptake capacity of 3.38 mg/g for the immobilization and 3.30 mg/g free biomass [25]. Biosorption of Cu(II) using Ca-alginate xerogel and alginate immobilized *Fucus vesiculosus*, optimum pH at 5.12 for Ca-alginate and 5.1 immobilized [29]. Adsorption of Cu(II) using alginate immobilized kaolin with removal percentage of 79.43% at pH 5[30] andadsorption of Cu(II) using alginate immobilized bentonite clay and optimum pH at 4-5 with initial concentration 400 mg/L and adsorption capacity of 53.86 mg/g and 52.39 mg/g [31]. Biosorption of Cu(II) and Pb(II) using loquat leaf (*Eriobotria japonica*) modified and optimum Cu(II) and Pb(II) ions at pH 6 [32].

Biosorption of Cd(II) ion using rice straw are obtained optimum pH at 5 with efficiency 47% [9]. Biosorption of Cd(II) on grapefruit peel optimum pH at 5 [3]. Biosorption of Zn(II) using powder Cow Hooves and pH absorption of Zn at pH 4 with adsorption efficiency of 94.5% [33] and biosorption of Zn(II) on *Undaria pinnatifida* obtained at pH 4[34].

## CONCLUSION

Alginate immobilized durian seed can be overcome the disadvantages of durian seed powder in acid solution. Ca-alginate immobilized durian seed studied in the form of a gel and dry bead and used for biosorption of metal ions Pb(II), Cu(II), Cd(II) and Zn(II). The heavy metal biosorption studied the effect of pH on the uptake capacity of heavy metals ion. The effectof pH to uptake capacity metal ions optimum obtained for each metal ionsare at pH 4-5 for Pb(II), pH 5-6 for Cu(II), pH 5-6 for Cd(II) andpH 4-5 for Zn(II) in alginate immobilized (dry and gel bead), non-immobilized and Ca-alginate. The order of uptake capacity for bio-sorbent is: dry bead> non- immobilized> gel bead> Ca-alginate.

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