Application of chitosan crosslink as selective adsorbent

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Abstract. A selective chitosan adsorbent may remove Cd2+ and Pb2+ ions in aquatic environment to reduce pollution. This study has applied crosslink chitosan to reduce Cd2+ and Pb2+ ions in water. The study is related to the searching of optimum condition with respect to citric acid and sodium tripolyphosphate concentrations in a batch method. The study also includes the determination of optimum pH and interaction study of complex molecule with either Cd2+ or Pb2+ ions in relation to competitive chitosan adsorption. The optimum pH is found at pH 5. The optimum concentration of citric acid with chitosan is found to be 1% (b/v). It is concluded that chitosan adsorbent is selective for Pb2+ over Cd2+ ions.

1. Introduction

Today’s world, heavy metal waste becomes a problem that must be addressed immediately because it gives a serious effect on the environmental balance, especially the aquatic environment. Waste is a disposal which the presence is not desired in the environment because it has uneconomical value, reduces environmental quality and able to interfere the life sustainability. On the other hand, the utilization of shrimp waste is less optimal where its use still limited as a mixture of low-grade crackers, shrimp paste or fodder. Therefore, one of alternatives to reduce shrimp waste and be more economic as well as efficient it is necessary to make alternative efforts to process shrimp waste into chitin and chitosan which has function as absorbers of harmful metals in industrial wastes such as Pb (II) ions and Cd ions (II). Chitosan is a material that has function as an adsorbent because of its biodegradable nature, means the ability to be decomposed by the environment (soil) after used [1]. Chitosan isolated from shrimp waste which potential to use as a material in the modification process because chitosan has -OH, NH2 and -NHCOCH3 groups which can form kelat, which is considerably available in the environment and nontoxic [2].

Modification of chitosan is one of alternative way to increase its stability in acidic conditions. Chemical modification of chitosan into chitosan gel able to incline its adsorption capacity. Chitosan forms a gel in an acidic atmosphere due to the formation of a three-dimensional link between chitosan molecules outspread across the entire volume of gel formed by bonding some water in it. Another advantage is that the gel form has a larger pore volume than the flake form, but the chitosan gel adsorption power is influenced by several factors, for instance concentration, temperature, pH, and polyelectrolyte [3].

The selection of citric acid (C6H8O7) based on the nature of chitosan in which the free amino group in chitosan causes its solubility properties is specific in acidic solutions and is an organic acid that can
dissolve chitosan which is easily found on the market. Acidity of citric acid is obtained from three carboxyl-COOH group which can release protons in solution. If this happens, the ion produced is citric ion. Citric ions can react with numerous metal ions to form citrate salts. Citric acid with its non-toxic properties and the presence of carboxylic groups which are owned by citric acid can form anions when dissolved in water, thus they can bind to chitosan to form cations[4].

Research on chitosan as an adsorbent has also been carried out by modifying chitosan using acetic acid as adsorbent of Cr (VI) metal in batik industry waste [5]. Modification of chitosan with acetic acid is also used for adsorbents to reduce levels of heavy metals Cu (II) [6], humic acid using as an adsorbent for Fe (III) metal ions [7]. Modification of chitosan with humic acid also to adsorb Fe (II) and Zn (II) [8]. Chitosan is modified with succinic acid for phosphate absorption (Juliana, 2014) and adsorption of chitosan with chitosan sulfate from shrimp shells to adsorb Ni (II) and Cd (II) [9; 10]. Based on these studies, recently, the use of chitosan with citric acid modification is still limited to the ability to adsorb metals separately or test their adsorption power only one heavy metal. The application of chitosan can be improved by physically or chemically modifying it to understand selectivity.

2. Research Method

2.1. Tools
The tools used include glassware, vacuum filters, Buchner funnels, stirrers, shakers, analytic scales, stopwatches, pH meters and Atomic Absorption Spectrophotometers (AAS)

2.2. Materials
The materials used in the study were chitosan (shrimp, DD 85%), citric acid (C$_6$H$_8$O$_7$), Pb(CH$_3$COO)$_2$, Cd(CH$_3$COO)$_2$ and distilled water.

2.3. Work Procedure

2.3.1. Cross-linkedChitosan synthesis. A total of 1000 mg of chitosan were dissolved in 10 mL of citric acid with various concentrations of 1%, 5%, 10%, 15%, and 20%, and then sterilized for 360 seconds. The chitosan gel formed was allowed to stand for 24 hours at room temperature. Chitosan citrate gel is formed beads using alkaline solution (KS). Then rinsed until neutral, in an oven at a temperature of 60° C until a constant weight is obtained.

2.3.2. Optimization of pH using KS Adsorbents. Weighed as much as 100 mg of chitosan crosslink adsorbent and interacted with 10 mL of Pb (II) ion and Cd (II) ion solution on a variation of pH 3-8 for 360 seconds, the filtrate was analyzed using atomic absorption spectrophotometer (AAS). The optimum pH obtained is used as a basis for further observations.

2.3.3. KS selectivity test for Pb (II) and Cd (II) ion solutions. A total of 100 mg of KS adsorbent (procedure 2) was interacted with 10 mL of Pb (II) and Cd (II) ion solutions for 360 seconds with a ratio of Pb (II): Cd (II), respectively 1: 0.1; 0.5: 1; 1: 1.5; 1: 2. Determination of the concentration of adsorbed metal ions, the distribution ratio and selectivity coefficient on the adsorption process of metal ions on KS adsorbents can be used the following equation:

\[
Q = \frac{(Co-Ca) V}{W}
\]

\[
D = \frac{Q}{Ca}
\]

\[
%A = \frac{(Co-Ca)}{Co} \times 100\%
\]

\[
\alpha = \frac{D_1}{D_2}
\]

Where Q states the number of metal ions adsorbed, D represents the distribution ratio and $\alpha$ represents the distribution coefficient.
3. Results and Discussion

Chitosan used in preparation of KS adsorbent is chitosan with 85% deacetylation degree, yellowish white, sieved with 100 Mesh particle size. to obtain KS adsorbent the size is smaller and uniform thus the trackpad of the surface is wider and causes the solubility of the KS incline. The selection of citric acid as a non-toxic solvent and has three carboxylic groups which could be strongly bonded with chitosan to form cations (Alamsyah, 2006).

![Image of Chitosan powder (A), chitosan citrate gel (B), KS Beads (C)](image)

**Figure 1.** Chitosan powder (A), chitosan citrate gel (B), KS Beads (C)

The solubility of chitosan due to protonation of chitosan amine groups by $H^+$ ions released by citric acid when dissolved in water and forming $NH_3^+$ ions thus chitosan can dissolve. One of the carboxyl groups of citric acid can form complexes with chitosan, the open group through ionic bonds and the second carboxyl group can form inter and intra covalent crosslinks.

![Diagram of Chitosan Reaction with Ion Citrate](image)

**Figure 2.** Illustration of Chitosan Reaction with Ion Citrate

Adsorption of Pb (II) and Cd (II) ions using KS adsorbent is strongly influenced by pH, the optimum result is optimum pH is pH 5. The same results are obtained by Masykur (2013). At low pH, adsorption occurs relatively small, because in this condition the active adsorbent KS tends to be in a protonated state and has a partial positive charge resulting in electrostatic repulsion and competition among the charge at the active site of KS adsorbent with a solution of Pb (II) and Cd ions (II). Optimum pH at pH 5, KS adsorbent in a neutral state, availability of KS adsorbent active groups in an effective state to adsorb Pb (II) and Cd (II) ion species. KS active adsorbent sites has function as electron pair donors, and there is a strong interaction between KS adsorbent Pb (II) and Cd (II) ions. After optimum pH is reached, adsorption declines even though the decline is less significant, this tendency occurs due to exceeding the price of Ksp ion Pb (II) and Cd (II) in a solution that even forms its hydroxide precipitate.
The results of the optimization of citric acid concentration showed that the concentration of citric acid affected the amount of adsorption of Pb (II) ions and Cd (II) ions. The optimum adsorption of Pb (II) and Cd (II) ions are in 1% citric acid concentration. NH$_3^+$ active group of optimum chitosan binds to 1% citric acid (KS). For KS 5%, 10%, 15% and 20%, gel formation has been shown, the higher the KS concentration, the gel that is formed becomes thicker which causes the adsorption capacity to be lower. The use of chitosan which does not form a gel is more flexible because it has larger pores and is easy to expand in the water medium so that it is able to adsorb a larger material compared to gel-shaped chitosan (Cahyaningrum, 2014).

The relationship of the percentage of Pb (II) and Cd (II) ions adsorbed to the KS adsorbent is shown in Figure 4. The selectivity coefficient ($\alpha$) of Pb (II) ions and Cd (II) ions when $\alpha \geq 1$ indicates that KS adsorbent is more distributed to Pb (II) ions which are intermediate acids compared to Cd (II) ions which are soft acids. Pb (II) ions without the presence of Cd (II) ion disturbers were adsorbed as much as 89%, while Cd (II) ions without Pb (II) ion interference were adsorbed as much as 80%. The percentage of adsorbed Pb (II) ion was 86% higher than the percentage of adsorbed Cd (II) ion was 64%. The probability of Pb (II) and Cd (II) ion bonding by KS can be seen in Figure 4. The free active site will be bound to chitosan and the adsorption mechanism through coordination covalent bonding

![Adsorption selectivity curves of Cd (II) by KS](image-url) **Figure 3.** Adsorption selectivity curves of Cd (II) by KS

![Selectivity adsorption between Pb(II) (black) and Cd(II) (red) ions of KS](image-url) **Figure 4.** Selectivity adsorption between Pb(II) (black) and Cd(II) (red) ions of KS
mechanism. NH2 which has a pair of free electrons will donate its free electron pair to the Cd (II) empty orbitals forming(NH2Cd)2+ as in Figure 5.

![Figure 5. Illustration of Chitosan Chelate Formation Reaction with Cd (II) [11]](image)

Adsorption capability in the competition between Pb (II) ions with Cd (II) can be seen based on the ion radius. Pb (II) ions are ionic larger than Cd (II) ion as the result they have relatively small electrostatic forces and cause the ability of Pb (II) ions to attract the surrounding water molecules to be weak. With the weak ability of Pb (II) in attracting water molecules, the hydration radius is smaller and the mobility or movement of Pb (II) ions in water is higher (fast), so that Pb (II) ions are easier to reach the surface KS adsorbent. In addition, the active group KS is classified as a strong base that will interact strongly with Pb (II) ions which are classified as intermediate acids compared to Cd (II) ions which are classified as weak acids in accordance with the HSAB concept of Pearson (1968). This proton ion Pb (II) which is larger than Cd (II) causes the nuclear attractiveness and nuclear effective charge of Pb (II) is greater, therefore it will make it easier for Pb (II) to induce cellulose nata which is non-polar and form a force electrostatic pull.

4. Conclusion and Recommendation

4.1. Conclusion

The results show that crosslink chitosan adsorption is better for Pb(II) ion rather than Cd (II) ion with respect to optimum pH, citric acid and tripolyphosphate concentrations, as well as interaction study between complex and both ions.

4.2. Recommendation

Further research is needed regarding optimization of interaction time.

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