Use of *Eichhornia crassipes* modified Nano-chitosan as a biosorbent for lead (II), cadmium (II), and copper (II) ion removal from aqueous solutions

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**Abstract.** Industrial waste in a major city poses a considerable threat to water environment from the accumulation of heavy metals. Additionally, uncontrolled growth of *Eichhornia crassipes* will also damage the water environment by lowering the levels of dissolved oxygen. Therefore, we conduct research to not only treat industrial waste in water but also reduce the population of *E. crassipes* in water. We made this biosorbent by mixing *E. crassipes* with nano-chitosan in various compositions. Its absorptivity was tested against single metal solutions of lead (II), cadmium (II), and copper (II) to get the best biosorbent composition. The chosen biosorbent then went through an adsorptivity test against a mixture of three solutions, with each test was carried at various pH. The best biosorbent composition is the mixture of 1 g of *E. crassipes* with 30 mL of nano-chitosan 0.01%, while adsorption tests in single or three metals solution show that the biosorbent performs better in neutral pH.

1. **Introduction**

Pollution is a major problem that plagued major cities in Indonesia such as DKI Jakarta, because it gave serious problems to people, as well as the environment, with one example being water pollution. One of the biggest contributors toward water pollution is a waste being disposed into the water without processing, especially industrial waste that still contains heavy metals. Such waste is hazardous because the heavy metals it contains can cause a massive degradation of water quality, as well as cause long-term harm to the residents due to the accumulation of heavy metals, especially on fish from such waters.

Heavy metal waste is one of the main problems plaguing DKI Jakarta. With many of industries disposing their waste into waters without proper processing, which cause severe pollution on waterways around Jakarta. It is a problem because many industries that did not properly process their waste before disposal have heavy metal content, which is known for their potential of causing long-term harm, and are already accumulated in sediments and water at worryingly high concentrations. Such as the waters in Western parts of Jakarta, the concentrations of metals Pb (Lead) are 8.49-31.22ppm; Cu (Copper) = 13.81-193.75 ppm, and Cd (Cadmium) = <0.001-0.47 ppm. It is a problem because the safe limit for Pb is 0 mg/L, or in other words, no lead is allowed at all, while for Cu is 1.3 mg/L and Cd is 0.005 mg/L [1]. It is a clear and present danger to residents because such metals in water will cause long-term harm to people.
On the other hand, water hyacinth (known to locals as eceng gondok. Biological name: *E. crassipes*) is a floating wild water flora that grows rapidly on freshwater surfaces, with growth rates as high as 220 kg/ha/day [2]. With its rapid growth and spread, water hyacinth can cause problems because an overpopulation of water hyacinth will bring harm, such as siltation of rivers due to remains of dead water hyacinths sinking into the river bottom, and also causes dissolved oxygen in the water to drop dramatically, which disturbs other organisms in the river.

While water hyacinth has been utilized for applications such as furniture, biogas, fertilizer, and livestock feeds, but there are still more potential applications for the water hyacinth. One of which is a biosorbent for absorbing heavy metals such as lead (Pb), cadmium (Cd), and copper (Cu). It is possible because of their cellulose content capable of absorbing such metals [3]. Cellulose itself is an organic compound consisting of long chains of glucose units which is bind by 1,4-β-glucosidic bonds, which can interact well with adsorbates thanks to the high amount of –OH [4]. The water hyacinth would then be modified with nano-chitosans to make a cost-effective biosorbent but is capable of adsorbing heavy metals effectively.

Chitosan and chitin are commercially valuable biopolymers which are commonly used in industry. Chitin is used as base ingredients in the industry such as pharmacology, agriculture, membrane makers, textile, cosmetics, etc. On the other hand, chitosan is produced from deacetylation process of chitin, which is commonly found as a major constituent of the exoskeleton of crustaceous marine animals [5]. Chitosan itself is also often used in water purification, a chelating agent, color binding agents, and also used as adsorbents of heavy metals.

Adsorption is a process where the dissolved substance in a solution is coagulated by the surface of the adsorbent, in which a chemical-physical bond is occurring between the substance and its adsorbent. Adsorption is divided into two kinds, physical and chemical adsorption (physisorption and chemisorption) [6]. This phenomenon should be distinguished from absorption, in which adsorption is a surface phenomenon while absorption is a volumetric phenomenon [7].

Physisorption is a reversible process involving van der Waals and hydrogen bonding with the adsorbent [8], while chemisorptions involves the formation of chemical bonding which consists of covalent and electrostatic bonding which makes the adsorbed substance harder to release and makes the process less reversible [9]. Factors affecting adsorption are as follows: contact time, the area of the adsorption media, adsorbate solubility, adsorbate molecule size, pH of the solution, and the temperature.

2. Experiment

2.1. Materials
Water hyacinths were picked up from a lake near the Faculty of Mathematics and Natural Science in University of Indonesia, Depok. Chitosan powder, glacial acetic acid, Pb(NO₃)₂, Cd(NO₃)₂.4H₂O, and Cu(NO₃)₂.3H₂O were supplied by Merck, Germany. All chemical reagents used in this experiment were of analytical grade and did not need further purification. Deionized water (Aquadest) was used as solvent for all solutions.

2.2. Biosorbent from water hyacinth synthesis
Water hyacinth was washed with aquadest to remove contaminants that stuck to the leaves and stem. It was then roughly blended using an ordinary blender and then dried at room temperature. After drying, it was then blended again until it became a fine powder. The powder was sieved with 60 mesh sieve to get a finer powder.

2.3. Nano-chitosan synthesis
Nano-chitosan was synthesized by dissolving chitosan powder in glacial acetic acid while stirring it with a magnetic stirrer for 3 h at room temperature. The glacial acetic acid is stirred first, with the
chitosan was slowly added to the solution. This process is done at room temperature (25°C). The stirrer is heated to facilitate dissolution of chitosan powder.

2.4. Biosorbent modification with nano-chitosan
The biosorbent was added into the synthesized nano-chitosan, and then stirred with magnetic stirrer. The resulting mixture was centrifuged, and the sediment was dried. Biosorbent mass was varied at 1 g, 0.75 g, and 0.5 g. The optimum mass was then determined.

10 mL nano-chitosan was then added for each biosorbent mass (1 g, 0.75 g, and 0.5 g) for each addition. The mixture was then stirred for 2 h, centrifuged, and the resulting residue was dried. The steps were repeated for two and three times. The maximum biosorbent mass was determined by Prestige 21 FTIR by Shimadzu, Japan, while the percent of nano-chitosan that interact with biosorbent was determined by gravimetry.

About 0.05 gr of biosorbent at each nano-chitosan addition was then put into a crucible, and burned in a furnace for two hours, then stored in a desiccator for 15 min. The crucible was then weighed and compared with empty crucible weight. The weight difference was the weight of the chitosan. The process is repeated until a constant weight is achieved.

2.5. Biosorbent application on single metal solution
Biosorbent application tests on the single metal solution were applied for Pb (II), Cd (II), and Cu (II). The single metal solutions were prepared as solution (50 mL) with each concentration of 1500 ppm, 300 ppm, and 600 ppm respectively. The application was done by inserting 0.1 g of the optimum biosorbent into the column. Then, 50 mL of metal solution was poured in. The solution which passed the biosorbent is then held in a container and then analyzed with Shimadzu AA-7000 AAS by Shimadzu, Japan. These procedures were done for Pb, Cd, and Cu metals.

2.6. Biosorbent application on mixture of metals solution
The application test was done by preparing a mixture solution by pipetting each 50 mL of Pb 4500 ppm, Cd 900 ppm, and Cu 1800 ppm solutions into a 150 mL volumetric flask, and then 100 mL of the solution was then used, so the concentration of each metal were the same with the single metal solutions. 50 mL of the mixture was then taken and flowed into a column with biosorbent. The solutions were held in a container and then analyzed by AAS. From this process, it was determined that the optimum composition is a mixture consisting of 1 g of E. crassipes in 30 mL of nano-chitosan 0.01%.

3. Results and Discussion

3.1. Results

3.1.1. pH variation Modified biosorbent adsorption on the single metal solution is done at pH 5 (acid) and pH 7 (neutral). Higher pH is not investigated due to formation of precipitate of metal ions, which cannot be adsorbed by the adsorbent.

3.1.2. Adsorption application for single metal solution According to Figure 1, it is known that the best adsorption is done against Pb metal, which is in accordance with HSAB (Hard-soft acid-base) theory that states hard acids are likely to interact with hard bases, so do the soft acids that are likely to interact with soft bases [10]. Because Pb and Cu are borderline acids, they are more easily bound to OH groups of cellulose and NH₂ groups of chitosan, which are both hard bases compared to Cd metal. However, Cd gives higher adsorption results than Cu which is not in accordance to the HSAB theory, because Cd is a soft acid and therefore would be less likely to bind with OH and NH₂. This error can be attributed to systematic errors in the experiment.
Figure 1. Adsorption percentage of single metal solutions against Pb, Cd, and Cu metals at various pH

Adsorption application for a mixture of three metals solution According to Figure 2, it is known that Pb has the best adsorption compared to Cd and Cu metals. The biosorbent also shows better adsorption against Cu metal compared to Cd metal, which is in accordance with HSAB theory, because Pb and Cu are borderline acids while Cd is a soft acid. In the mixture solution, the adsorption capacity is decreased compared to single solution, because there are more metals in the solution to be adsorbed. Also, it is shown that the adsorption process is better at pH 7 (neutral) because at acidic pH, there are H⁺ ions that can degrade the adsorption capabilities of the adsorbent by making the active sites less available for metal ions [11].

Figure 2. Adsorption percentage of mixed metal solutions against Pb, Cd, and Cu metals at various pH

4. Conclusion
It is concluded from our research that it indeed is possible to synthesize a biosorbent from nano-chitosan modified water hyacinth to adsorb heavy metals. The synthesized biosorbent performs best in neutral pH compared to acidic pH, because at acidic pH, the H⁺ ions will degrade the adsorption abilities of the biosorbent. While in basic pH, the biosorbent cannot function properly because basic pH will cause the formation of solids which cannot be adsorbed. During adsorption tests, the adsorbent
adsorbs Pb better than Cu and Cd, which can be attributed to HSAB theory, and the adsorbent capacity in mixture solution is less than single metal solutions because there are more kinds of metals to adsorb.

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