Application of Rice Husk Immobilized in Chitosan-Alginate Beads as a Biosorbent for Acid and Basic Dye Removal

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Abstract—In this research, the biosorbents were prepared based on immobilization technique. The two forms of rice husk, raw rice husk and modified rice husk powder, were entrapped in chitosan-alginate bead. The different amounts of rice husk powder (0.5%, 1.0%, and 2.0% (w/v)) were mixed with 2% (w/v) alginate solution. The bead was formed by dropwise into chitosan solution containing calcium chloride solution with various ratios (1:4, 1:1, and 4:1). For examining dye removal efficiency, two color groups, basic dye (BB09, BR09) and acid dye (AB25, AR18) were applied. The beads (2.0 g) were incubated in 20 ml dye solution containing 50 mg/L of each dye. The results revealed that the suitable condition for beads preparing was 2.0% (w/v) rice husk in 2% (w/v) alginate solution and dropwise into chitosan solution containing calcium chloride solution with ratio 4:1. The bead containing modified rice husk showed the highest removal efficiency for both basic and acid dye. The basic dyes removal efficiency, BB09 and BR09, were observed at 99.00%±0.11%, and 85.07%±1.03%, respectively. For acid dye, AB25 and AR18, which were, 77.15%±1.30% and 84.69%±3.08%, respectively. As the results implied, application of modified rice husk immobilized in chitosan-alginate bead as a biosorbent for dye removal could be an alternative way for utilization of agricultural waste. These could eventually lead to reduction of chemical requirement for wastewater treatment in textile industry.

Keywords—alginate, chitosan, dye removal, risk husk

I. INTRODUCTION

The synthetic dyes have been extensively applied in several industries such as textile, leather, paper, food, and cosmetic [1]. According to the differences in their charges, synthetic dyes are typically divided into three categories: cationic dyes, such as basic dyes, anionic dyes, such as reactive, direct, and acid dye, and non-ionic dyes, such as disperse dyes [2]. Since dyes’ complex aromatic structure and synthetic origin make them non-biodegradable and stable under a variety of situations, dyeing effluents have been known as one of the most problematic wastewaters [1, 3]. The effects of dyeing effluents not only their physical and chemical properties, but also possibly lead to adverse health impact on aquatic communities in the receiving natural waterway [4, 5].

Numerous approaches, including filtration, chemical oxidation, chemical coagulation, precipitation, adsorption, have been tested for solving this problem. Among them, adsorption technique is frequently used for dye removal because it is easy to use, highly effective, and produces no harmful byproducts [5]. Recently, agricultural wastes, including rice bran, wheat bran, maize cob, are increasing popular as biomaterial for production of suitable adsorbents for the purpose [4, 6]. Rice husk is one of the most easily accessible and environmentally favorable materials [1]. Their main components, i.e., cellulose, hemicellulose, and lignin, exhibit negative charges, which facilitate absorption of many positively charged pollutants [5]. Although, rice husk has been reported as an attractive bio-based adsorbent material for the removal of many dyes, heavy metals and pesticides [1, 4], its low density as well as high silica contents in their outer structure could be an obstacle for improving their adsorption capacity [7]. To overcome disadvantages, the immobilization technique to form beads of rice husk with other biopolymers could be applied. Many biopolymers such as alginate, carboxymethyl cellulose, chitosan, have been suggested as an immobilizing agent [7, 8]. Chitosan is one of the commonly biopolymers used for dye removal. Due to it composes with amino and hydroxyl functional groups, it could absorb both negatively charged and positively charged of dyes containing in textile wastewater [7, 8]. Alginate, a natural anionic polysaccharide extracted from brown seaweed, is also usually recommend as biopolymer for develop biosorbent using in wastewater treatment [8, 9]. Alginate consisting of (1→4)-D-mannuronic acid (M) and α-(1→4)-L-guluronic acid (G) [9]. Several previous studies suggested that cross-link of alginate and chitosan in hydrogel beads were environmentally friendly adsorbents which could be successfully applied for removal of various dyes from aqueous solutions and textile effluents [9, 10]. However, there was few studies present the application of agricultural waste with these biopolymers to enhance the adsorption capacity [11].

For the present research, various conditions for preparing suitable rice husk immobilized in chitosan-alginate beads were tested. In addition, Acid and Basic dyes removal efficiency of the beads in synthetic wastewater was observed and recorded. A new biosorbent prepared from rice husk entrapped in chitosan-alginate beads suitable for removal of both positively and negatively charged residue dyes in textile wastewater were expected.

II. METHODOLOGY

A. Materials

Chitosan flakes (95% deacetylation) were purchased from Chitosan Seafresh Co., Ltd. Alginic acid was supplied from Sigma. A commercial dye, Basic Blue 9 (BB9), Basic Red 9 (BR9), Acid Blue 25 (AB25), and Acid Red 18 (AR18), were obtained from dyeing industry. All chemical reagents were analytical grade.

B. Preparation of Rice Husk and Modified Rice Husk Powder

Rice husk and modified rice husk were prepared for use in dye removal. The 20 g of rice husks were weighed, washed three to four times in distilled water, dried in an oven at 105 °C for three hours, and then ground into a powder using a blender. In order to prepare modified rice husk by using a chemical treatment, hydrochloric acid (HCl) was selected for
this purpose. Rice husk powder was mixed with 1% (v/v) of hydrochloric acid (HCl) solution. The ratio of rice husk powder to hydrochloric acid solution was 1:10 w/v. The suspension was stirred for 1 h, then the rice husk power was removed by centrifuging, and then washed with distilled water 3–4 times, dried in an oven at 105 °C for 3 h.

C. Preparation of Raw Rice Husk Bead and Modified Rice Husk Bead

The bead containing rice husk were prepared based on immobilization technique. As show in Table 1, three different amounts of grounded rice husk (0.5%, 1.0%, and 2.0% w/v) were mixed with 2% w/v Na-alginate solutions. In order to prepare bead suitable for dye removal, the raw rice husk and the modified rice husk was applied for this test. The mixture was dropwised into 2% (w/v) chitosan solution containing 2% (w/v) CaCl₂ with various ratios (1:4, 1:1, and 4:1). The beads were formed and left 6 hours in 2% (w/v) CaCl₂ solutions for hardening purpose. The beads were thoroughly rinsed with distilled water to remove residue CaCl₂ and stored in distilled water at 4 °C.

Table 1. Formation ratios of rice husk immobilized in chitosan-alginate bead

<table>
<thead>
<tr>
<th>Condition</th>
<th>Chitosan: CaCl₂</th>
<th>Raw rice husk or modified rice husk powder (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A11</td>
<td>1:4</td>
<td>0.5</td>
</tr>
<tr>
<td>A12</td>
<td>1:4</td>
<td>1.0</td>
</tr>
<tr>
<td>A13</td>
<td>1:4</td>
<td>2.0</td>
</tr>
<tr>
<td>A21</td>
<td>1:1</td>
<td>0.5</td>
</tr>
<tr>
<td>A22</td>
<td>1:1</td>
<td>1.0</td>
</tr>
<tr>
<td>A23</td>
<td>1:1</td>
<td>2.0</td>
</tr>
<tr>
<td>A31</td>
<td>4:1</td>
<td>0.5</td>
</tr>
<tr>
<td>A32</td>
<td>4:1</td>
<td>1.0</td>
</tr>
<tr>
<td>A33</td>
<td>4:1</td>
<td>2.0</td>
</tr>
</tbody>
</table>

D. Determination of Basic and Acid Dye Removal Efficiency

For the purpose, each type of rice husk beads (2.0 g) was contracted to 20 mL solution of synthetic wastewater containing 50 mg/L of dye for 24 h in an orbital incubator shaker at 150 rpm and 35 °C. After adsorption experiments, absorbance of the solutions was determined using a UV/VIS spectrophotometer at wavelength 600 nm, 507 nm, 665 nm, and 540 nm for Acid blue 25, Acid red 18, Basic blue 9, and Basic red 9, respectively.

E. Data Analysis

Dye removal efficiency was calculated using the following formula:

\[ \% \text{Dye removal} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \]

where \( C_0 \) and \( C_e \) represented the concentrations of dye (mg/L) in the solution at time, \( t = 0 \) and at equilibrium (e), respectively.

All statistical analysis was conducted using a statistical package SPSS 23. For all experiments, results from triplicate samples were obtained. Mean, standard deviation the measurements were reported. For comparison purpose, ability of varying types of rice husk beads for dye removal in synthetic wastewaters was compared using one-way analysis of variance (one-way ANOVA) at 95% confidence.

III. RESULTS AND DISCUSSION

A. Bead Morphology

An initial objective of this research was to develop biosorbent by immobilizing rice husk in chitosan-alginate bead. As shown in Fig. 1, after dropwise alginate solution containing different amount of grounded rice husk (0.5%, 1.0%, and 2.0%; w/v) into 2% (w/v) chitosan solution containing 2% (w/v) calcium chloride with various ratios (1:4, 1:1, and 4:1), the beads obtained all conditions were completely formed a spherical shape. These results due to a cross-linking between adjacent biopolymer chain, α-L-guluronic acid, and bivalent cations in aqueous media, such as calcium ions [10]. After reaction with calcium ions, alginate can form gels so that it can retain its shape and size unchanged. The rice husks were entrapped in a solid core of alginate and coated with chitosan membrane.

![Fig. 1. Morphology of the prepared Bio composite beads with different amount of rice husk powder (a) 0.5% w/v; (b) 1.0% w/v; (c) 2.0% w/v.](image)

As reported in Table 2, the diameter of beads prepared from various conditions, A11–A33, were observed between 2.89±0.33–3.25±0.25 mm. The diameter of beads was significantly increase with the increasing composition of chitosan in bead. The chitosan membrane could be completely formed outer side of alginate bead. These results probably due to the strong electrostatic interaction of the polycationic structure of chitosan, mainly amine groups, and carboxylic groups which exhibited negative charges of alginate [11]. Thus, increasing of chitosan in bead composition probably led to increasing of outer layer of the bead.

![Fig. 2. SEM images of chitosan-alginate containing rice husk. (a). surface structure (500x magnification); (b). The porosity of rice husk powder immobilized in chitosan-alginate bead (magnification 200 times).](image)
B. Basic Dye Removal Efficiency

To examine the efficiency of rice husk beads for basic dye removal, two different basic dyes, Basic Blue 09 and Basic Red 09, were applied for this experiment. The rice husk prepared in two forms, raw rice husk and modified rice husk, was loaded in the chitosan-alginate bead under 9 different conditions. After each bead type contract to the synthetic wastewater containing 50 mg/L of each dye for 24 h in an orbital incubator shaker at 150 rpm, 35 °C. The dye removal efficiency was detected by using a UV/VIS spectrophotometer. The results obtained from these tests are shown in Fig. 3.

According to the findings, all of the raw rice husk beads and modified rice husk beads effectively absorbed the Basic Blue 09. For the raw rice husk beads, the color removal efficiency was observed in the range of 85.23%±1.92%–96.80%±0.14%. In the case of modified rice husk bead, the dye adsorption efficiency was examined in the range of 88.37%±0.23%–99.60%±0.11%. These also accord with other research, which showed that raw rice husk and modified rice husk can be applied for the adsorption of Basic Blue 09 (known as Methylene Blue), in aqueous solutions [3]. Comparing the dye removal efficiency of beads loaded with different types of rice husk, there were significantly differences observed. These results are probably due to the fact that the rice husk surface was chemically modified with HCl. The surface impurities like natural fats, waxes, and low molecular weight lignin compounds coated on the rice husk surface were removed. This can improve the surface roughness, increase the surface area, and improve adsorption properties [13]. The number of carboxyl groups and hydroxyl groups that act as proton donors contained in modified rice husk was higher than observed in raw rice husk. As a result, positive dye ions in Methylene blue could be coordinated with deprotonated OH and carboxyl groups of rice husk [14].

After contracting with Basic dyes, the adsorbent’s surface exhibited significant changes that demonstrated that there had been an ion exchange between the adsorbent and adsorbate. As shown in Fig. 5(a), after being contracted to synthetic wastewater containing a basic blue color, BB09. The bead color was changed from light to blue. The result was also observed in a basic red color, BR09. The bead color was changed to red (Fig. 5(b)). This result indicated that the positively charged molecules of basic dye molecules could interacted with negatively charged bead components, including alginate, chitosan, and rice husk.

Similarly, an experiment was performed in Basic Red 09 by using raw rice husk and modified rice husk beads prepared from various conditions as an absorbent. As shown in Fig. 4, all of the beads obtained from raw rice husk and modified rice husk immobilized in chitosan-alginate also showed efficiency for removal of Basic Red 09 in synthetic wastewater. For the raw rice husk beads, the color removal efficiency was observed in the range of 42.68%±1.53%–84.50%±0.33%. In the case of the modified rice husk bead, the dye adsorption efficiency was examined in the range of 45.22%±1.96%–85.07%±1.03%. The dye removal efficiency of raw rice husk beads was less than that of modified rice husk beads. This may be due to the modification of the rice husk, which can lead to an increased capacity for adsorption, that is, the amount of the adsorbate molecule adsorbed on the surface. These results agree with another study which reported that the modification with acid can enhance the adsorption of the cationic dye, Basic Red 4G, on the surface of these modified rice husks with electrostatic attraction force [13].

Another important finding was that the rice husk beads obtained from various conditions, A11–A33, had significant differences in the removal efficiency of both dyes, Basic Blue 09 and Basic Red 09. As illustrated in Figs. 3–4, the basic dye removal efficiency of rice husk beads is trending to increase with increasing amounts of rice husk and chitosan in the beads. The bead prepared from 2.0% w/v of rice husk mixed with 2% (w/v) alginate solution and dropwise into chitosan solution containing calcium chloride solution with a ratio of 4:1 showed the highest efficiency for the removal of two Basic dyes. For basic Blue 09, which was 96.80%±0.14%, and 99.60%±0.11%, for raw rice husk beads and modified rice husk beads, respectively. In the case of Basic Red 09, which was 81.45%±0.33%, and 85.07%±1.03%, for raw rice husk beads and modified rice husk beads, respectively. These results indicated that varying amounts of rice husk and chitosan played an important role on basic dye removal efficiency. Many researchers reported that rice husk is good
adsorbent for basic dyes [7, 14, 15]. Increasing amounts of rice husk probably led to an increase in binding sites for positively charged on basic dye molecules. These results are agreement with previous researches, which found a proportional relationship between the amount of chitosan and absorption. The increasing amounts of chitosan result in an increase in electrostatic bonding, which increases the absorption of dyes [16].

C. Acid Dye Removal Efficiency

Acid dyes were categorized as anionic dyes, which exhibit acidic properties and are negatively charged [17]. In this research, the rice husk and modified beads prepared from various conditions were contracted with the synthetic wastewater containing 50 mg/L of acid dye, Acid Blue 18 and Acid Red 25, under similar conditions as the basic dye removal test.

As shown in Figs. 6−7, the efficiency of rice husk beads for the removal of two acid dyes, Acid Blue 18 and Acid Red 25, were observed in the range of 27.72%±3.09%−72.85%±3.02%, and 4.38%±2.50%−75.31%±2.36%, respectively. While the efficiency of modified rice husk beads for the removal of such dyes was presented in the range of 55.81%±6.06%−77.15%±1.30%, and 9.27%±2.90%−84.69%±3.08%, respectively. These results indicated that the modified rice husk beads were a better adsorbent than rice husk beads.

[Graphs showing dye removal efficiency]

Rice husk typically has the following chemical components: 32.24% cellulose, 21.34% hemicellulose, 21.44% lignin, 1.82% extractives, 8.11% water, and 15.05% mineral ash (which has a silica value of approximately 96.34%) [4]. Hydrolysis of rice husks is best accomplished through acid treatment. The acid is able to separate lignin and other organic components from rice. The enhancement of the adsorption capacity of acid treated rice husk might also be due to the protonation of the adsorbent surface. The surface became positively charged, and electrostatic attraction developed between the positively charged surface and the negatively charged dye molecule, which further increased the amount of dye adsorbed [4, 18].

In addition, the results showed that the nine forms of rice husk bead, A11−A33, were significantly different in their acid dye removal efficiency. At the confidence level of 95%, the bead obtained from the A33 condition was the most effective in removing acid dye. The highest percentage of dye removal efficiency is 77.15%±1.30% for Acid Blue dye and 84.69%±3.08% for Acid Red dyes. This is most likely because chitosan has a unique molecular structure that enables the amino groups on its main chain to protonate in an acidic environment, which accounts for these results [2].

Adsorption is a surface phenomenon where molecules, ions, and atoms from dissolved solids, liquids, and gases stick to the active/binding sites of a solid substance known as the adsorbent [17]. As shown in Fig. 8, the changing of bead color could be observed after the beads were exposed to acid dye solution.

[Images showing bead color changes]

The bead color was changed from the original, clear color to light blue (Fig. 8(a)) and light pink (Fig. 8(b)). These results implied that the acid dyes were mainly attached to the rice husk particles loaded in the chitosan-alginate bead. These findings contrasted with those made in the basic dye removal study. The adsorbent’s surface characteristics, such as surface area, surface charge, and particle size, influence the adsorption capacity [16]. Alginate, a naturally anionic biopolymer, is the solid core of the bead. While the acid dye is an anionic dye, it is thus hard to be adsorbed on those surfaces [13, 16]. However, the modified rice husk immobilized in the chitosan-alginate bead could be applied to remove both basic and acid dyes in an aqueous solution.

IV. CONCLUSION

The main goal of this study was to developed a biosorbent from rice husk. The immobilizing agents, including chitosan and alginate, were selected for entrapment of raw rice husk and modified rice husk in a bead form. In addition, the basic and acid dye removal efficiency of rice husk beads prepared from various conditions were determined in synthetic wastewater. The results of this investigation showed that the chitosan-alginate beads containing rice husk could form and exhibit both basic and acid dyes removal efficiency. For the best results, chitosan-alginate bead containing 2.0% of modified rice husk mixed with 2%(w/v) alginate solution and dropwise into a chitosan solution containing calcium chloride solution with a ratio of 4:1 exhibited the highest adsorption.
capacity. The basic dye removal efficiency of BB09 and BR09 were observed at 99.60%±0.11% and 81.45%±0.33%, respectively. For acid dye, AB25 and AR18, were 77.15%±1.30% and 84.69%±3.08%, respectively. The results of this research the support idea that rice husk immobilized in chitosan-alginate beads could decrease the affinity of dye molecules. The new sorbent prepared from biomaterials which were environmentally friendly product could be applied for removal both Basic and Acid dyes. In addition, the sorbent obtained in bead form could be easily to remove from medium after treatment process.

**CONFLICT OF INTEREST**
The authors declare no conflict of interest

**AUTHOR CONTRIBUTIONS**
The study’s conceptualization and design, data collection, analysis and result interpretation, as well as the paper preparation, all bear the author’s complete responsibility.

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