Efficiency Improvement of Some Agricultural Residue Modified Materials for Textile Dyes Absorption

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Abstract. In this work, the adsorption efficiency was investigated of some agricultural residue modified materials as natural bio-adsorbents which were rice straw (Oryza sativa L.) and pineapple leaves (Ananas comosus (L.) Merr.) for the removal of textile dyes. Reactive dyes were used in this research. The improvement procedure of agricultural residue materials properties were alkali-acid modification with sodium hydroxide solution and hydrochloric acid solution. Adsorption performance has been investigated using batch experiments. Investigated adsorption factors consisted of adsorbent dose, contact time, adsorbent materials and pH of solution. The results were found that rice straw had higher adsorption capacity than pineapple leaves. The increasing of adsorption capacity depends on adsorbent dose and contact time. Moreover, the optimum pH for dye adsorption was acidic range because lowering pH increased the positively charges on the adsorbent surface which could be attacked by negatively charge of acid dyes. The agricultural residue modified materials had significant dye removal efficiency which these adsorbents could be used for the treatment of textile effluent in industries.

1. Introduction
Among the consequences of this rapid of mankind, society, science and technology growth is environmental disorder with a big pollution problem. Toxic organic and inorganic pollutants are compounds of great concern due to toxicity, persistence, bioaccumulation in animals and persist in living organism, which cause several environmental problems to environment [1]. Industrial developments in recent years have left their impression on the environmental society. Many industries, such as textile, paper, plastics and printing industry are using more than 100,000 commercially available dyes to color their products and thus produce wastewater containing organics with a strong color, where in the dyeing processes the amount of dye lost wastewater is up to 50% of the dye [2]. One of the important classes of the pollutants is dyes, and once they enter the water it is no longer good and sometimes difficult to treat as the dyes have a synthetic origin and a complex molecular structure which makes them more stable and difficult to be bio-degraded [3]. Wastewater remediation is considered to be one of the main approaches for water recycling that provides the deficiency of water in different regions in daily life. Of these dyestuffs, 5–10% is lost in industrial effluents, which is released into water resource such as river, seas and groundwater. Global and local agencies have therefore established certain limits on the quantities of dyestuffs being discharged into environment when the concentration is as low as 1 ppm [4].

The removal of dyes from waste effluents becomes environmentally important because even a small quantity of dye in water can be toxic and highly visible. Therefore, efficient techniques for the removal of dye from wastewater, such as biological processes, photo catalytic degradation, coagulation, chemical oxidation processes and adsorption, which depend on the types of dyes to be
removed, their composition, concentrations and production flow into the wastewater. Adsorption is a physical–chemical treatment, which is used as top quality treatment procedures for the removal of dissolved organic pollutants like dyes from industrial waste water. Adsorption is defined as concentration of materials on the surface of solid bodies (adsorbents). Adsorbents are mainly derived from natural and unnatural sources such as zeolites, charcoal, clays and other waste resources. Natural bio-adsorbents prepared from waste resources used include coconut shell, rice husk, petroleum wastes, tannin-rich materials, sawdust, fertilizer wastes, chitosan, algae, fruit wastes, rice straw and pineapple leaves etc. [1, 5].

Natural bio-adsorbents are comprised of lignocellulosic matters, could be an excellent adsorbent for wastewater treatment due to low cost, biodegradability, eco-friendliness and high stable nature to most organic solvents. Furthermore, these types of lignocellulosic matter have high density of hydroxyl groups and easy to modify with specific functional groups, e.g., carboxyl, amino, sulfo and cyclodextrin groups for removal of specific pollutants [6]. Nevertheless, natural bio-adsorbents have not always a very high adsorption capacity, which is one of the main restrictions for its use in water remediation. However, some research report that the use of simple chemical modifications was increase the adsorptive capacity without increasing the cost of final product and, thereby, its widespread use may not be impeded. Consequently, natural bio-adsorbents are chemically treated with chemical reagents in low cost solutions such as acids or bases, causing an increase in the pollutant-removing capacity. Several studies report that chemical modifications of bio-adsorbents may introduce functional groups within the structure of the adsorbents or increase their porosity, with an increase in their adsorption capacity [7]. The agricultural residues materials for removing effluent waste are rice straw and pineapple leaves as adsorbent. Rice straw has 69.2% cellulose, 10.2% hemicellulose and 4.9% lignin [8]. Pineapple leaves have 43.5% cellulose, 21.9% hemicellulose and 13.9% lignin [9]. Rice straw and pineapple leaves have the advantage of high lignocellulosic material, large-scale production, low cost, and easy access.

Thus, the aim of this study was to investigate the adsorption efficiency of some agricultural residue modified materials as natural bio-adsorbents which were rice straw and pineapple leaves for the removal of textile dyes from aqueous solution. The influence of process parameters including: adsorbents dose, contact time, bio-adsorbent types and pH were studied.

2. Materials and methods

2.1. Preparation of modified materials

Bio-adsorbent materials used in this study as rice straw and pineapple leaves were collected from a farm in Kanjanaburi, Thailand. Firstly, the materials were washed with distilled water to remove dust and soluble impurities and grinded using a laboratory mill. Secondly, the ground bio-adsorbent materials were soaked in distilled water for several times until the water was colorless. Following, the ground bio-adsorbent materials were dried at 85 ± 2°C for 12 hours and sieved into size of about 0.5 mm.

The bio-adsorbent materials are modified with hydrochloric acid (HCl) and sodium hydroxide (NaOH) at difference concentrations (0.1%, 0.3% and 0.5%). The ground bio-adsorbent materials were soaked in the solution at room temperature for 2 hours and filtered off. The modified bio-adsorbent materials were washed with distilled water for several times until the pH of the filtrate reached between 6 – 7. Finally, the modified bio-adsorbent materials were dried at 85 ± 2°C for 12 hours and stored in plastic bags at room temperature and dry place for further use.

2.2. Adsorption experiment

Adsorption experiments were carried out using rice straw and pineapple leaves as bio-adsorbents. The influences of several parameters (adsorbent/dye solution ratio, contact time and pH) were studied in batch experiment. In order to establish the effect of bio-adsorbent (g) : dye solution (mL) ratios as 1:5, 1:10, 1:15 and 1:20 g/mL were used, with 0.1% reactive blue dye solution. The effect of contact time on the adsorption capacity of rice straw and pineapple leaves bio-adsorbent was studied for 30, 60, 90, 120, 150, 180 and 240 min at an initial concentration of 0.1% reactive blue dye solution. The optimal
conditions of adsorbent/dye solution ratio and contact time were performed for dye adsorption of bio-
adsorbents (rice straw and pineapple leaves) and modified bio-adsorbents (modified rice straw and
modified pineapple leaves). The effect of pH on the adsorption of dye solutions was studied in a range
of 4–8 with resolution of ± 0.05 pH. The solutions were pH adjusted with 0.1 M HCl or 0.1 M NaOH
using a pH meter to perform the measurements. In all experiments, different bio-adsorbents were
added to dye solution as wastewater sample. The mixtures were stirred at 500 rpm with magnetic
stirrer at room temperature. The bio-adsorbents were separated by filtration through, Whatman
qualitative No. 4, filter paper. The concentration of residual dye concentration was determined using
UV-VIS spectrometer at suitable wavelength (λ=597 nm for dye solution). All measurements were
carried out in triplicate and the results were averaged. The removal efficiency percentage was
calculated from the following equation:

\[
\text{Removal dye (\%)} = \left( \frac{C_i - C_t}{C_i} \right) \times 100
\]

where \( C_i \) and \( C_t \) are the reactive blue dye concentrations at the beginning of an experiment and that
at time \( t \), respectively.

3. Results and discussions

3.1. Effect of bio-adsorbent:dye solution ratios and contact times

The effect of bio-adsorbent:dye solution ratios on removal percentage of reactive blue dye was shown
in figure 1. The percentage of removal gradually increased with enhancing bio-adsorbent dosage. Reactive blue dye removal efficiency for all types of bio-adsorbents was found to increase with
increasing amount of rice straw and pineapple leaves. The increase of removal efficiency was possibly
because of increasing availability of reactive blue dye capturing sites, adsorption sites of bio-
adsorbent and surface area of bio-adsorbent with increased amount of bio-adsorbents [6, 10].
Moreover, the chemical structure of lignocellulosic materials as bio-adsorbents consists of many
reactive chemical functional groups for removal of specific pollutants such as alcoholic and phenolic
hydroxyl, carboxyl, carbonyl, ether, ester groups, etc. [11]. The maximum percentage removal of
reactive blue dye from aqueous solution by rice straw and pineapple leaves were 1:10 of bio-
adsorbent:dye solution ratio.

Contact time represents the time of interaction between the bio-adsorbent and reactive blue dye in
the solution (figure 1). Generally, increasing the contact time between the bio-adsorbent and the
reactive blue dye increases the amount of reactive blue dye uptake from their solutions. The reactive
blue dye uptake was rapidly within the first period and reached an equilibrium state at 120 min due to
the large number of the free active adsorption sites on the bio-adsorbents and the relatively high
concentrations of the reactive blue dye in the solution [12].

The optimum bio-adsorbent: dye solution ratios and contact times were selected as 1:10 and 120
min for other experiments.

3.2. Effect of different bio-adsorbent types

The chemical modifications play an important role to improve the adsorption capacity of the biomass.
The comparison of all pretreatments is displayed in figure 2. The results showed that the enhancement
in the uptake capacity of rice straw and pineapple leaves was achieved when NaOH and HCl were
used for pretreatment. The chemical modifications of bio-adsorbents may introduce functional groups
within the structure of the adsorbents or increase their porosity, with an increase in their adsorption
capacity [7]. The rice straw modified with 0.5% HCl and pineapple leaves modified with 0.5% HCl
showed much improvement in the uptake capacity of bio-adsorbents. The possible explanation for
significant improvement in the uptake capacity of bio-adsorbents for reactive blue dye is that upon
modification with inorganic acids might rupture the lignocellulosic fibers and reduce of impurities
from the lignocellulosic fiber, which could release polysaccharides, natural fat and wax from
lignocellulosic fiber surface, thus revealing chemically reactive functional groups and offer increase
porosity and surface area for adsorption and also display high affinity for certain reactive blue dye [13,
14]. The rice straw modified with 0.5% HCl and pineapple leaves modified with 0.5% HCl were selected for the effect of solution pH experiments.

**Figure 1.** Effect of bio-adsorbent: dye solution ratios and contact times onto rice straw and pineapple leaves as bio-adsorbents for reactive blue dye adsorption.

![Graph showing removal rate of reactive blue dye on rice straw and pineapple leaves](image)

**Figure 2.** Effect of different bio-adsorbent types for reactive blue dye adsorption.

![Bar chart showing removal rate of reactive blue dye under different modified conditions](image)

3.3. **Effect of pH**

The effect of initial solution pH on the adsorption of reactive blue dye onto rice straw modified with 0.5% HCl and pineapple leaves modified with 0.5% HCl was examined and the results are presented in Figure 3. The pH value determines the surface charge of the adsorbent and the ionic form of the dyes molecules, both influencing the amount of reactive blue dye adsorbed by bio-adsorbent. Removal efficiencies were the greater at acidic pH because the surface of the bio-adsorbent become positively charged from protonation of hydroxyl and carbonyl groups on the surface which easily attract the negatively charged of reactive blue dye (anionic dye) ions and remove them from water [6, 15].
4. Conclusions

The adsorption efficiency of rice straw and pineapple leaves on chemically modified materials as natural bio-adsorbents which were for the removal of reactive blue dye from aqueous solution. The influence of process parameters including: adsorbents dose, contact time, bio-adsorbent types and pH were studied. The optimum of bio-adsorbent : dye solution ratios and contact times were 1:10 and 120 min. The rice straw modified with 0.5% HCl was the outstanding bio-adsorbent for the removal of reactive blue dye from aqueous solution. The acidic pH solution indicated the greater removal efficiencies.

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