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Removal of Reactive Dye Using New Modified Chitosan-Pandan Sorbent

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This research aims to synthesise the modified Chitosan-Pandan by performing impregnated approach at which the extracted polyphenols of pandan oil was served as stabiliser. The extractions of pandan leaves were carried out using maceration process whereby ethanol (95 vol%) was used as solvent. The characterisations of the modified Chitosan-Pandan were examined using Fourier transform infrared spectroscopy (FTIR). A batch adsorption of Reactive Black 5 (RB5) from aqueous solution using the modified Chitosan-Pandan were conducted under different range of retention time (0 - 40 min), initial mass concentration dyes (0.1 - 1.0 g/L), pH solution (5 - 11), temperature (25 - 80 ± 1 °C) and dosage of sorbent (0.1 - 1.0 g). The optimum adsorption was achieved up to 99.9 % within 30 min, 0.2 g/L initial dye concentration, 0.1 g dosage of sorbent, pH 7 and at room temperature. Compared to raw chitosan, the modified Chitosan-Pandan was proven to have better percentage removal of RB5.The results obtained shows that the modified Chitosan-Pandan has great potential to be used as a powerful novel sorbent.

1. Introduction

There is increasingly global demand on synthetic dyes in various high-technology industrial fields such as textile, leather tanning, paper printing, food, plastic, cosmetic and pharmaceutical (Yagub et al., 2014). Reported that an annual discharged of dyes in wastewater up to 100 t/y (Mu and Wang, 2016). This water pollution will cause adverse impact to environmental. Dyes are easily visible even in low concentration that causes reduction of sunlight transmission and oxygen in the water. There are about more than 100,000 synthetic dyes commercially available in industries, which may possess potential toxic, carcinogenic, mutagenic and tetratogenic compounds (Mendes et al., 2015). Synthetic dyes have complex aromatic and amine structure which is chemically stable, persistence and non-biodegradable. If dye of wastewater is not treated properly this will lead to accumulation in soil, plant, animal and human body (Vakili et al., 2015). It also can cause dysfunctional of kidney, reproduction system, liver, brain and nerves system to human being (Yagub et al., 2014).

Reactive black 5 (RB5) dye is one of the most commonly used in industries for dyeing of cellulosic fibres, wool and nylon. RB5 contains active groups such as azo, anthraquinone, triarylmethane, phthalocyanine, formazan and oxazine. These active groups form covalent bond with fibres during dyeing process. Based on Syamimi et al. (2016) study, the RB5 have shown good stability in terms of pH, thermal and either exposed or unexposed to the light. It also reported that RB5 has high solubility in water (Mohamed and Walaa, 2016).

In previous studies, chitosan received great attention for reducing dyes from aqueous solution (Liu et al., 2015). The reason is that, chitosan possesses high affinity for most dyes, chemical stability, good chelating agent and high reactivity (Kashif et al., 2016). Chitosan is known as a second abundance polymer, non-toxicity, biodegradability, biocompatible nature and low cost which makes it high potential as useful sorbent in wastewater treatment. Chitosan also consist copious amino and hydroxyl group. However, chitosan is insoluble in water, therefore losses physical structure, and its low mechanical strength and poor acid

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resistance are also not very satisfactory. Chitosan is insoluble in water due to intermolecular and intramolecular hydrogen bonds.

In this study, the biodegradable modified Chitosan-Pandan sorbent was used for dye adsorption in aqueous solution. The modified Chitosan-Pandan was synthesised by impregnated with extracted pandan-polyphenols. These polyphenols assist to break the intermolecular and intramolecular hydrogen bonds through binding with amino group of chitosan (Hu and Luo, 2016). It was reported that pandan leaves contains polyphenols acid (gallic acid, ferulic acid and cinamic acid), flavonoids (catechin) and amino acid (glutamic acid, aspartic acid, threonine, serine, histidine, alanine, and proline) (Ningrum and Schreiner, 2014). Natural polyphenol has relatively high capacity of antioxidant and ability to scavenge free radicals (Jin and Russell, 2010). The antioxidants help to increase hydroxyl group towards backbone of chitosan (Hu and Luo, 2016). Extracted pandan-polyphenols is believed to increase the adsorption capacity by improving chitosan physicochemical properties. Moreover, the synthesis involved simple and economic preparation. This sorbent is also biodegradable and friendly environment since both materials come from natural sources.

2. Methodology

In this research, there were two types of sorbents used which are modified and unmodified chitosan. The chitosan was modified using extracted pandan oil through wet impregnation method. The extraction pandan were attained through maceration technique whereby ethanol (95 vol%) was used as solvent. The modified chitosan was referred as modified Chitosan-Pandan. To investigate the adsorption performances of Reactive black 5 (RB5) onto modified Chitosan-Pandan sorbent, adsorption reactions will be conducted at different range of contact time 0 - 120 min, initial pH solution 5 - 11, temperature reaction 30 - 80 °C, initial RB5 dye concentration 0.1 - 1.0 g/L and dosage of sorbent 0.1 - 1.0 g. The raw chitosan will be tested under the same operational condition of modified Chitosan-Pandan in order to compare the performances adsorption between before and after modification.

2.1 Materials and reagent

Fresh pandan fibres (Pandanusamaryllifolius) were purchased from a local market at Taman Universiti, Skudai, Johor, Malaysia. Chemical that were used in this experiment are raw chitosan, liquefied ethanol (C_2H_6O, 95 vol%), Black reactive 5 (BR5,$C_{26}H_{21}N_5Na_4O_{19}S_6$) dye powder, 0.1 M solution of sodium hydroxide (NaOH), 0.1 M solution of hydrochloric acid (HCl), nitrogen gas (N_2), distilled water, deionised water and filter paper (pore size = 125 nm). Other chemicals were purchased from Sigma Aldrich of analytical grade and used as received without further treatment.

2.2 Synthesis of modified Chitosan-Pandan sorbent

Roughly 200 g of fresh pandan leaves were cleaned and cut into pieces (approximately 3 cm). Then, we placed it in an oven at 45 °C for 48 h. The dried pandan leaves obtained were grounded and sieved (particles size = 150 μm). 5 g of meshed pandan were immersed into 100 mL of ethanol for 24 h. The solution was filtered in order to remove any residual meshed pandan. After that, the permeate liquid collected from bottom of filter paper were placed on the hot plate at 80 °C to remove the remaining ethanol. After several minutes, the liquefied obtained known as extracted pandan oil.

In order to synthesise the modified chitosan, 0.07 g of chitosan was dissolved in 50 mL of extracted pandan oil for 24 h and placed it at room temperature. Then, the mixture was filtered and washed several times with deionised water that pH was regularly checked until it achieved neutral. The wet sediments were scraped off carefully from top of filter paper and dried at 60 °C for 24 h. Finally, the hybrid Chitosan-Pandan sorbent obtained was stored into the desiccator to preserve the moisture content of the sorbent.

2.3 Characterisation

Before and after modification of chitosan was analysed using a Fourier transform infrared spectrophotometer-FTIR (IRTrace-100). The samples were recorded at room temperature with spectral region of 4,000 to 400 cm^{-1} and resolution at 2 cm^{-1}.

2.4 Experiment of adsorption

Reactive dye that has been selected in this adsorption study was the Reactive Black 5 (RB5) with initial concentration set at 0.1 g/L of stock solution. The analytical grade of 0.1 M of HCl and NaOH solutions were used for pH adjustment throughout the experiment. For batch adsorption experiment, the condition was set up by which 0.10 g of Chitosan-Pandan that weighed was added into a 30 mL of 0.10 g/L RB5 dye with shaking speed 200 rpm at pH 7 and room temperature. The experimental for retention time were carried out until it reached the equilibrium value. The repetition procedures were performed for different effect of pH solution (5 -

11), temperature (25 - 80 °C) and dosage of sorbent (0.1 - 1.0 g). After the adsorption reaction, the samples were filtered to separate the supernatant from sorbent particles and analysed through U.V-Vis Spectrometry (Optizen Pop) at the maximum wavelength which was 595 nm.

3. Results and discussion

3.1 Characterisation

The FTIR spectroscopic of raw chitosan and modified Chitosan-Pandan are presented in Figure 1. Apparently, after modification of chitosan, the peak has shown significant change. Peak at 3,300 cm^{-1} indicates that presence of N-H groups (amine) (Tafarah et al., 2016). N-H groups were found in both raw and modified of chitosan with peak at 3,311 cm^{-1} and 3,325 cm^{-1}. However, modified chitosan shown the peak obviously compared to raw chitosan. This may due to modified chitosan has higher number of N-H groups than raw chitosan. Broad stretching vibration bands range from 3,200 cm^{-1} to 3,400 cm^{-1} indicates that presence of O-H groups (hydroxyl) (Patpen et al., 2014). Modified Chitosan-Pandan shown broad band at 3,325 cm^{-1} which corresponding to strong O-H stretching. The sharp peak at 1,637 cm^{-1} and 1,425 cm^{-1} may be due to C=C or N-C stretching of modified Chitosan-Pandan. This revealed presence of O-H and N-H groups in modified Chitosan-Pandan which is important for adsorption reaction. These groups were used to interact with RB5 ions in order to remove the dye ion in aqueous solution.

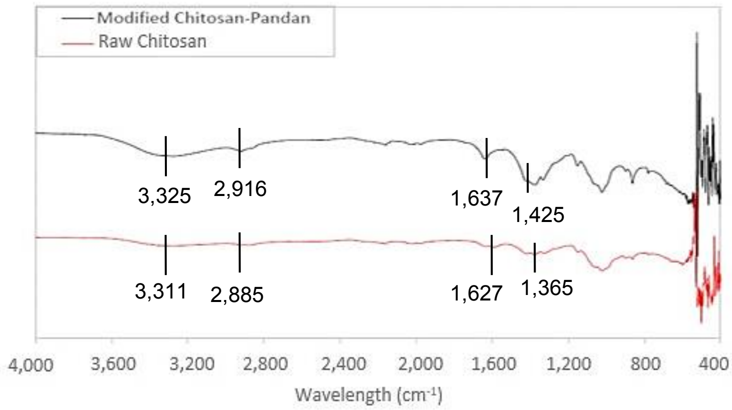


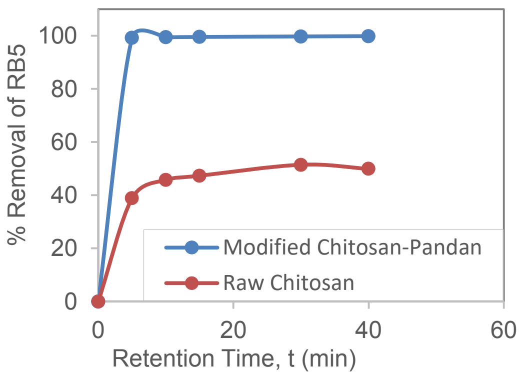
Figure 1: FTIR spectra for raw chitosan and modified Chitosan-Pandan

3.2 Effect of reaction time

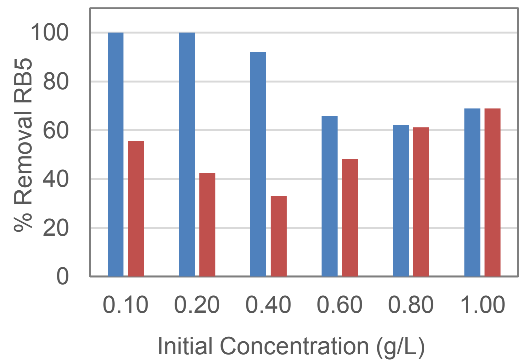
The effect of retention time on the adsorption of RB5 onto modified Chitosan-Pandan and raw chitosan is shown in Figure 2(a). As can be seen, the percentage removal of RB5 for modified chitosan began to rise dramatically until it reached at 5 min (99.3 %) and at 30 min until 40 min it remains stable (99.8 %). As for raw chitosan, the adsorption was slowly increased at 5 min (38.9 %) until 15 min (47.4 %) and reached to constant at 30 min (51.5 %). The modified Chitosan-Pandan was found to achieve faster adsorption with higher percentage removal of RB5 as compared to raw chitosan due to higher number of N-H group exhibit on surface. This is corresponding to the result FTIR obtained (Section 3.1). This positive charge N-H group is important in adsorption reaction, which assists to attract RB5 anionic dye molecules with electrostatic forces in aqueous solution (Hassan, 2015). For that reason, RB5 dyes molecules rapidly attached on surface binding site of modified sorbent at first 15 min. Rate adsorption was stable after 30 min indicate that there are no ion dyes available to adsorb since the efficiency removal achieved almost 100 %. Based from the result, the optimum retention time of modified Chitosan-Pandan obtained is 30 min.

3.3 Effect of initial concentration of dye

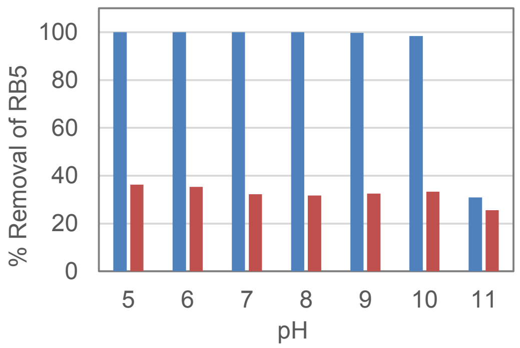
Figure 2(b) shows the percentage removal of RB5 by difference range of initial mass concentration dyes. The percentage removal of RB5 was increased up to 100 % from 0.1 g/L and remained the same at 0.2 g/L. At 0.4 g/L the percentage removal decreased slightly with value 92.1 %. As initial concentration increased at 0.6 g/L and 0.8 g/L the efficiency continually dropped to 65.8 % and 62.2 %. At 1.0 g/L the adsorption increased up to 68.9 %. As for the raw chitosan, as the first three initial concentration increased the adsorption capacity gradually declined which are 0.1 g/L (55.5 %), 0.2 g/L (42.4 %) and 0.4 g/L (33.0 %). From 0.6 g/L to 1.0 g/L the efficiency was rising with value 48.2 % and 68.9 %. The percentage of dye removal will decrease with increasing initial mass concentration of dye due to increasing number of molecule dyes that retained in aqueous solutions. The experimental result shows that the most optimum initial mass concentration of dyes value for modified Chitosan-Pandan is 0.2 g/L.



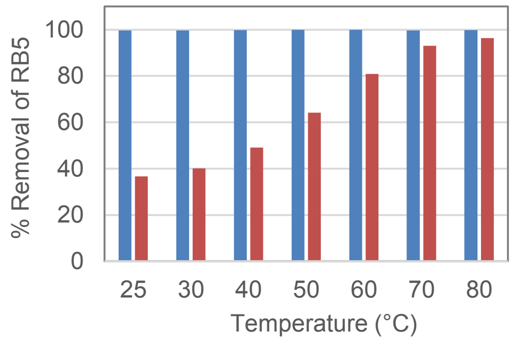
(a) Retention time (dosage = 0.1 g, conc. = 0.1 g/L, V = 30 mL, pH = 7, T = 25 °C)



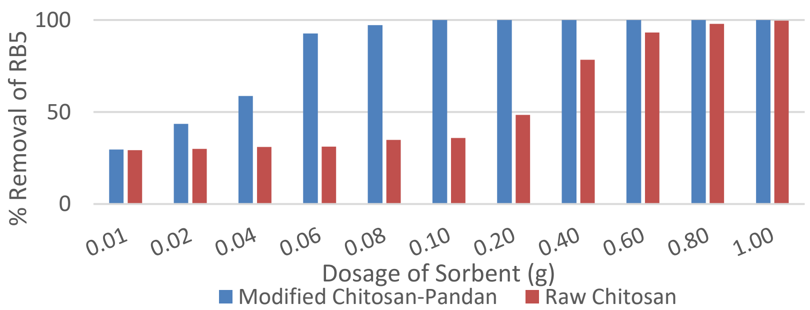
(b) Initial dye concentration (time = 30 min, dosage = 0.1 g, V = 30 mL, pH = 7, T = 25 °C)



(c) pH (time = 30 min, dosage = 0.1 g, conc. = 0.2 g/L, V = 30 mL, T = 25 °C)



(d) Temperature (time = 30 min, dosage = 0.1 g, conc. = 0.2 g/L, V = 30 mL, pH = 7)



(e) Dosage of sorbent (time = 30 min, conc. = 0.2 g/L, V = 30 mL, pH = 7, T = 25 °C)

Figure 2: Effect of (a) retention time, (b) initial dye concentration, (c) pH, (d) temperature and (e) dosage of sorbent on removal of RB5

3.4 Effect of pH

Percentage removal of RB5 from aqueous solution using modified Chitosan-Pandan and raw chitosan are shown in Figure 2(c) with different range of pH from 5 to 11. The pH value plays an important role in determining the ability of adsorption process. According to the graph, from pH 5 until pH 10, the adsorption capacities of RB5 onto modified Chitosan-Pandan were achieved over 100.0 %. As reaching up to pH 11 the rate of adsorption of RB5 showed a sudden drop to 31.0 %. On the other hand, raw chitosan adsorption capacity at pH 5 was about 36.2 %. As pH increasing the efficiency adsorption were decreased at pH 6 (35.3 %) and until pH 10 (33.3 %) there is no significant change. At pH 11 there was slightly decrease which is about 25.6 %. Compared to raw chitosan, the modified chitosan-pandan had achieved the pH stability.

Whereas, at pH range from 5 to 10, the capacity of adsorption does not seem to be influenced as it retained almost 100 %. In contrast, the highest adsorption capacity of raw chitosan was at pH 5 which is about 36.2 %. Based on previous studies, there reported that the chitosan is only give high adsorption under acidic condition due to presence of -OH and $-NH_3$ groups (Mu and Wang, 2016). At strong alkaline which is pH 11, both raw and modified chitosan the adsorption abrupt decreased to 25.6 % and 31 %. Aqueous solution under strong alkaline will produce an excessive OH^- ions. Since RB5 is anionic dye, There will be mutual repulsion between dye ions and OH^- ions (Mokhtar et al., 2008). This causes the reduction of adsorption of RB5 onto sorbent. According to result obtained, this can be stated that the modification is a success as modified chitosan achieved pH stability compared to raw. The experimental result shows that the optimum pH value for modified Chitosan-Pandan is pH 7.

3.5 Effect of temperature

This section discussed on effect of temperature on the adsorption of RB5 in the range 25 to 80 °C and the results are presented in Figure 2(d). At ambient temperature, modified Chitosan-Pandan sorbent achieved removal efficiency of RB5 up to 99.7 % and remains unchanged until 80 °C. On the raw chitosan side, temperature from 25 °C until 80 °C, there were gradually rose with value up to 36.6 % and 96.4 %. This shown that the temperature does not influence the adsorption RB5 efficiency of modified chitosan, since there is no significant change as the temperature increased. As for the raw chitosan, the temperature give great impact to adsorption dyes whereas temperature increased the percentage removal was also increased. This may due to as temperature increased, the energy released towards dye ions to increase its mobility in aqueous solution (Salwa and Amani, 2012). As particles starts to move fast, this suppress the adsorption rate of sorbent. Based on results obtained, the optimum temperature for modified Chitosan-Pandan is 25 °C

3.6 Effect of dosage of sorbent

Figure 2(e) shows the percentage removal of RB5 by different range of dosages of adsorbent. The percentage removal of RB5 increased from 55.1 % to 95.3 % as the dosage was increased from 0.01 g to 0.04 g. At 0.05 g, the efficiency reached up to 99.9 % and stays constant up to 1.00 g. The percentage of dye removal increases with increasing dosage due to increasing of the sorption sites that available on the surface of sorbent by increasing the amount of the adsorbent. This is the reason where modified and raw chitosan adsorption increased as dosage of sorbent increased. The modified chitosan achieved almost 100 % adsorption capacity with dosage 0.10 g. Raw needed more dosage in order to achieved same adsorption capacity which is about 1.00 g. The effect of dosage of modified chitosan for adsorption RB5 was economical because even with lower dose of sorbent it able adsorbs more dye RB5 compared to raw chitosan (Yagub et al., 2014). The experimental result shows that the most optimum dosage value for modified Chitosan-Pandan is 0.1 g.

4. Conclusions

Based on the result obtained, the modified Chitosan-Pandan shows a good adsorption performance compared to raw chitosan in term of retention time, initial dye concentration, pH, temperature and dosage of sorbent. The optimum condition for adsorption RB5 onto hybrid Chitosan-Pandan is achieved up to 99.9 % within 30 min, 0.2 g/L initial dye concentration, pH 7, at room temperature and 0.1 g dosage of sorbent. In conclusion, the modification of chitosan was revealed to be successfully and can be used a new renewable sorbent for the removal of reactive dye from textile wastewater.

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