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Polyethylenimine Modified Sugarcane Bagasse Adsorbent for Methyl Orange Dye Removal

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This study is investigated the potential of sugarcane bagasse, an agriculture waste as adsorbent for the removal of methyl orange dye from aqueous solution. Numerous research had been done in preparing low cost adsorbent from agricultural by-products. Activated carbon undoubtedly is the most prevailing adsorbent because of its high surface area adsorption capacity, and degree of surface reactivity. The activation process during preparation of activated carbon is normally been performed at high temperature (i.e. higher than 500 ºC) and involved with a harsh chemical. This study investigated the potential of modified sugarcane bagasse with polyethylenimine (PEI) for removal of methyl orange (MO) dyes. The effect of PEI modified sugarcane bagasse adsorbent parameter on the efficiency of dyes removal including contact time, initial dye concentration, adsorbent dosage, temperature and pH have been investigated. The optimum result for MO dye removal achieve up to 82.0 % for parameters, contact time (240 min), initial dye concentration (0.01 g/L), adsorbent dosage (0.15 g/50 mL), temperature (30 ºC) and pH (7). The maximum percentage dye removal of MO dye was reached at contact time 240 min with percentage 82.78 % for 240 min and initial dye concentration 0.05 g/L at percentage 82.78 %. Based on the optimum result, the adsorbent was efficient in decolorised diluted solution. PEI modified sugarcane has high potential as low cost adsorbent for wastewater treatment containing dyes.

1. Introduction

In textile industry, dyes are important in dying process. Dye is difficult to biodegrade because it contains complex aromatic molecular structures which make it stable in water. Dye also can bring a bright and firm colour to materials. Textile industries consume large quantities of water and chemicals, especially in dyeing and finishing process. The effluent that discharge from the industries contains highly colours synthetic dye which can affect the water bodies although at low concentration because dyes possess as high water solubility. Dyes also can cause various diseases such as allergy, dermatitis, skin irritation and cancer because it is resistant to natural biological degradation (Tahir et al., 2016). It is needed to remove dye from wastewater. There are several methods has been used to improve a sustainable method for dye removal from industries effluents such as biological treatment, adsorption, chemical oxidation, photolysis, suspended or supported photocatalysis degradation and electrophotocatalysis (El-Gamal et al., 2015). Among those methods, adsorption is the most efficient, economical, low cost, and low energy requirement. In the previous study, activated carbon is the most common adsorbent used to remove dyes (Zhang et al., 2012). The widespread use of activated carbon in industries is restricted due to high cost and difficulties in removal from the sludge (El-Gamal et al., 2015).

The new alternative adsorbent was studied in order to replace activated carbon such as biomaterial which is byproducts or agriculture waste material. Agriculture waste material was economic and eco-friendly adsorbent because of their unique chemical composition, availability in abundance, renewable, low in cost and more efficient (Sud et al., 2008).

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In previous study, there are several types of agriculture waste were used as adsorbent to remove dye such as sugarcane bagasse, wheat bran, straw and pomelo peel. Most of the adsorbent were modified with physical and chemical method to increase the adsorption capacity. The chemical treat that used to modify the adsorbent is hydrochloric acid (HCl), sodium hydroxide (NaOH), and potassium hydroxide (KOH) (Sajab et al., 2013). Sugarcane bagasse is one of agriculture waste that used to produce adsorbent. The sugarcane bagasse contains carboxylic and hydroxyl group which functions as in adsorbing dye molecules by ion exchange phenomena or by complexation. The sugarcane bagasse can be a cheap, attractive and effective adsorbent for dye removal from wastewater (Zaheer et al., 2014).

2. Materials and methods

2.1 Preparation of adsorbent

Sugarcane bagasse (SB) were obtained from the night market, Taman Sri Pulai, Johor. The SB was dried in the oven at 70 ºC for overnight. After that, the SB were ground and sieved to at range 300 - 250 µm. Prior to modification, the SB were modified with Polyethylenimine (PEI) based on the previous report (Sajab et al., 2013). 10 g of SB was treated with PEI solution (5 % w/v) at 65 ºC for 6 h. The mixture was washed several times using deionised water and dried in the oven at 60 ºC for 24 h. The adsorbent was stored in desiccators for further use.

2.2 Dye solution preparation

In this study, Methyl Orange (MO) dye were prepared and diluted according to the initial concentration required. The concentrations of solution were measured using Uv-Vis spectrophotometer at a λ_{max} of 465 nm.

2.3 Adsorption experiment

The dye removal experiments were carried out at a batch test in 100 mL Scott bottle. Each test was prepared in 50 mL of a dye solution with desired initial concentration and pH by diluting the stock dye with distilled water. The pH of the solution was adjusted using NaOH and HCl solution. After that the adsorbent was added into the solution and the mixture was shaken at 180 rpm. The experiment was done by varying the amount of adsorbents (0.05 – 0.15 g), contact time (60 – 300 min), the concentration of dye solution (0.01 – 0.1 g/L), temperature (30 – 70 ºC) and pH (5 - 9). The mixture was withdrawn from the shaker and filter to separate the adsorbent from the solution. The solution was analysed using UV-VIS spectrophotometer to determine the dye concentration. Then, the percentage (%) of dye removal was calculated according to Eq(1):

$$\text{Percentage of dye removal (\%)} = \frac{C_o - C_f}{C_o} \times 100\ \% \tag{1}$$

where C_o and C_f are the initial and equilibrium concentration of dye (g/L).

3. Result and discussion

3.1 Characterisation of PEI modified sugarcane bagasse

One of important characterisation of PEI modified sugarcane bagasse is Brunauer Emmett Teller (BET) analysis which include the porosity characteristic such as surface area, volume and size. This characteristic evaluated by Nitrogen desorption analysis method. Figure 1(a) show adsorption and desorption isotherm of nitrogen on PEI modified SB. According to IUPAC, the isotherm of nitrogen on the PEI modified SB is classified into Type IV (Thommes et al., 2015). This isotherm deviation indicates the significant existence of mesopores. The pore size distribution of the mesoporous PEI modified sugarcane bagasse was derived from the adsorption branch or desorption branch of the isotherm. Figure 1(b), have been determined by BJH method for PEI modified SB. According to BJH method, the pore size 2 – 50 nm is categories as mesopores and the pore width of PEI modified SB in the range (Storck et al., 1998).

FTIR spectrometry of raw SB and PEI modified SB are shown in Figure 2. From Figure 2(a), the raw SB show the intense band at around 3,335.94 cm^{-1} which assigned to the O-H stretching vibration. The adsorption bands at 2,903.88 and 2,901.95 cm^{-1} characterised the C-H stretching vibration. The C=O bond on the raw SB was presence at 1,722.46 and 1,637.84 cm^{-1}. In Figure 2(b), the presence of N-H functional groups and C-H stretching vibration was confirm by bands at 1,505.47 and 2,896.17 cm^{-1}. There are broad band in range of 3,600 - 3,200 cm^{-1} which mean the overlap of the N-H bond of amino group with the O-H bond of hydroxyl groups (Wong and Martincigh, 2013).

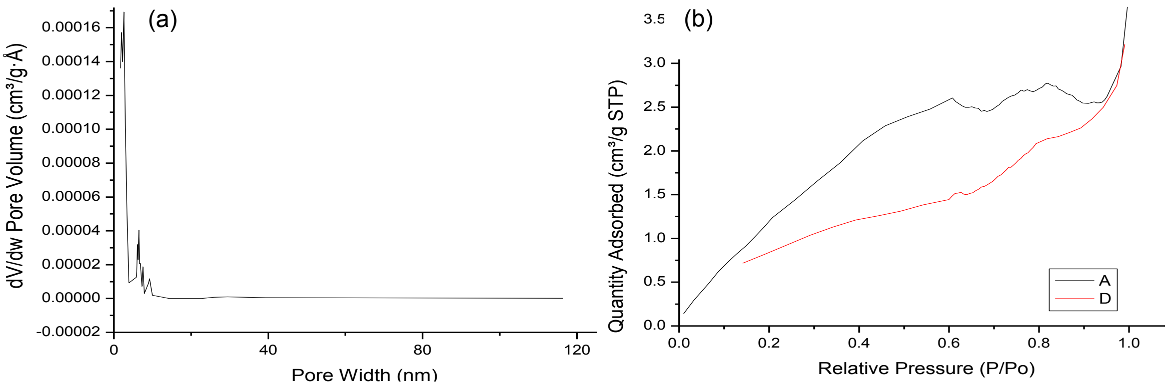

Figure 1: (a) Adsorption and desorption isotherm of nitrogen on PEI modified sugarcane bagasse, (b) Pore size distribution of PEI modified sugarcane bagasse

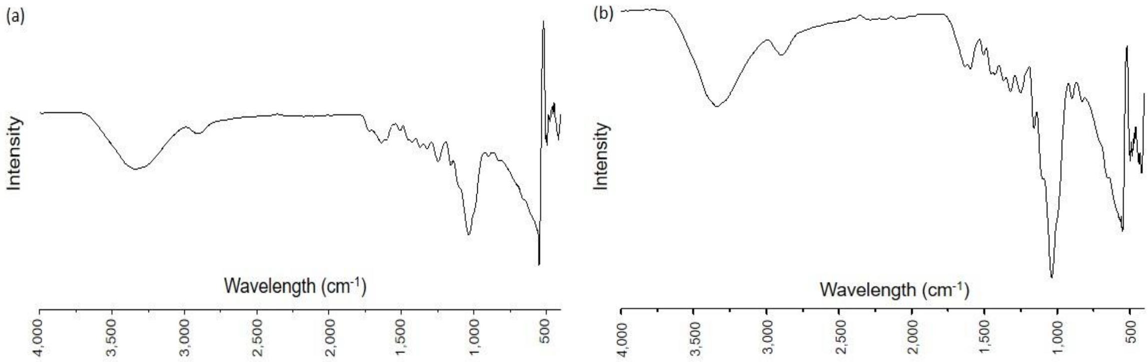

Figure 2: FTIR analysis of (a) raw SB and (b) PEI modified SB

3.2 Parameter effects

3.2.1 Effect of contact time

The contact time of dye removal was varied from 60 – 300 min. Figure 3 shows the effect of contact time on adsorption of MO dye. The best contact time for dye removal is 240 min with the percentage of 87.5 %. The percentage of dye removal increased from 82.73 to 87.24 % (60 to 240 min) but decrease at 300 min (82.78 %). The percentage of dye removal is still higher than 80 % even though recorded a decrement at 300 min. This happens when the surface adsorptions become saturated and the uptake rate was slow down. Then the transport rate was controlled from the exterior to the interior site of the adsorbent (Tao et.al. 2015). The other factor that effects to the result of adsorption is the aggregation of dye molecules with the increase of contact time which makes the adsorbent structure is difficult to diffuse deeper at the higher energy site. The aggregation negates can influence contact time because of the pores get filled up and begin to offering the resistance to diffusion of aggregated dye molecules in the adsorbent (Sharma and Kaur, 2011). Therefore, the equilibrium time of this adsorption process is 240 min because the maximum adsorption is attained during this period.

3.2.2 Effect of adsorbent dosage

Figure 4 demonstrates the result of percentage of MO dye removal with the effect of adsorbent dosage from 0.05 to 0.15 g. Form the graph, when the adsorbent dosage increase, the percentage of dye removal also increase. The percentage of dye adsorbed was more than 60 % when the adsorbent dosages increase from 0.05 g until 0.15 g. The factor that indicates the increased of dye adsorption with the increase of adsorbent dosage can be explained by the increased of surface area and the greater number of exchangeable sites available for interaction with dye molecules (Bazrafshan et al., 2014). The increase of adsorbent dosage also contributes to the increase of surface area along with the increased of active functional group that available on the adsorption site (Hamzeh et al., 2012).

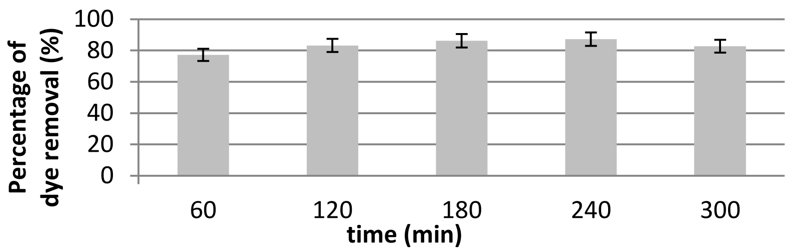

Figure 3: Effect of contact time on adsorption of Methyl Orange dye (adsorbent dosage = 0.1 g/ 50 mL, pH = 7, dye concentration= 0.05 g/L, temperature= 30 °C)

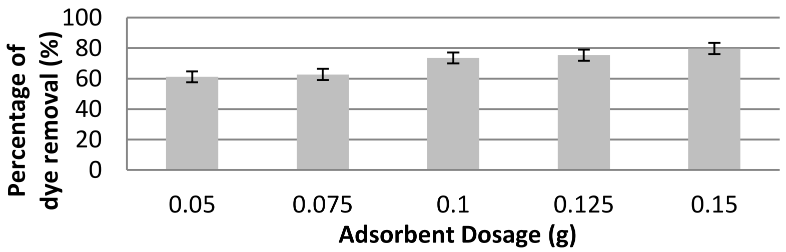

Figure 4: Effect of adsorbent dosage on adsorption of Methyl Orange dye (contact time = 240 min, pH = 7, dye concentration = 0.05 g/L, temperature = 30 °C)

3.2.3 Effect of initial dye concentration

To determine the effect of initial dye concentration, initial MO dye concentration was varied from 0.01 to 0.15 g/L. The result can be clearly seen in Figure 5, that increasing of initial dye concentration of MO had cause the decreasing of the percentage of dye removal from 82.78 to 64.24 % which shows that the adsorption process depends on the initial dye concentration. The adsorption capacity of the initial dye concentration also decrease when the concentration increase. This may be due to the exits reductions in immediate solute adsorption which owing to the lack of available active site that required for the high initial concentration of MO. The existed of reduction in immediate solute adsorption which is owing to lacking of the available active site that required for the high initial concentration of MO dye one of the factor may contribute to the decrease of dye adsorption (Amin, 2008).

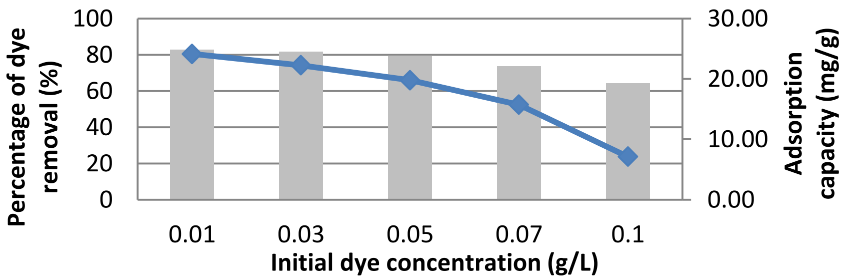

Figure 5: Effect of dye concentration on adsorption of Methyl Orange dye (contact time = 240 min, adsorbent dosage = 0.1 g/50 mL, pH = 7, temperature = 30 ºC)

3.2.4 Effect of temperature

The effect of temperature is one of the parameter that need to studies for the optimise adsorption process. In this study, the temperature was varied from 30 to 70 ºC by using water bath shaker. From the graph in Figure 6, the results show that when the temperature increases the percentage of dye removal was decreased from 75.44 to 17.98 %. This indicated that the adsorption reaction of MO dye onto the PEI-modified sugarcane is exothermic (Li et al., 2016). The best temperature for MO dye removal is at 30 ºC. The factor that indicates the decrease is due to the weak binding forces between the dye molecules and an adsorbent surface which may be break at high temperature (Sharma and Kaur, 2011). The others factor that effected the decreased of adsorption process is the equilibrium position in relation to the exothermic of the process and the swelling capacity of adsorbent (Aljebori and Alshirifi, 2012).

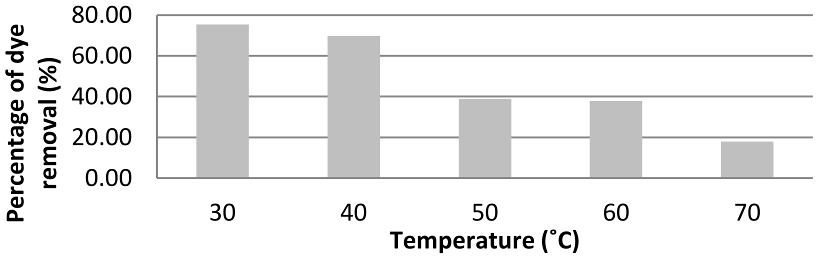

Figure 6: Effect of temperature on adsorption of Methyl Orange dye (contact time = 240 min, adsorbent dosage = 0.1 g/50 mL, pH = 7, dye concentration= 0.05 g/L)

3.2.5 Effect of pH

The pH is one of an important parameter of adsorption process because the solution pH can affect the surface charge of the adsorbent along with the degree of ionisation of the different pollutants and dissociation of functional groups on the active site of adsorbent. The result of percentage of MO dye removal using PSB showed in Figure 7. When the pH increased (5 – 7), the percentage of dye removal also increase from 61.50 to 78.32 %. The percentage of dye removal decreased from 78.32 to 11.32 % when it reaches pH 8 to 9. From the result, at acidic stage give an increased adsorption process because of the binding site of adsorbent would closely associate with the hydrogen ions which act as bridging ligands between adsorbent surface and dye molecules (Bazrafshan et al., 2014). The other factor that effect the decreases of the adsorption of MO dye onto PEI modified SB especially at pH 9 is because of the great amount of OH^- competing with anionic MO molecules (Sajab et al., 2013).

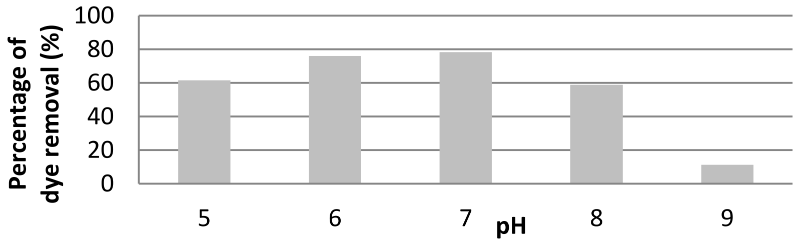

Figure 7: Effect of pH on adsorption of Methyl Orange dye (contact time= 240 min, adsorbent dosage = 0.1 g/ 50 mL, dye concentration = 0.05 g/L, temperature = 30 °C)

3.3 Comparative study

For the purpose of comparative study, the raw SB has been investigated at the optimum parameters of PEI modified SB. Figure 8, show the comparison result of raw SB and PEI modified SB and it was found that PEI modified SB have high percentage of MO dye removal compared to raw SB. The surface groups of raw SB was negative charge and the negative charge of dye molecules may due to the coulombic repulsion (Basik et al., 2009). The presence of PEI on the SB can enhance the performance of SB at adsorption process because of the positive charge PEI (Öztekin et al., 2002).

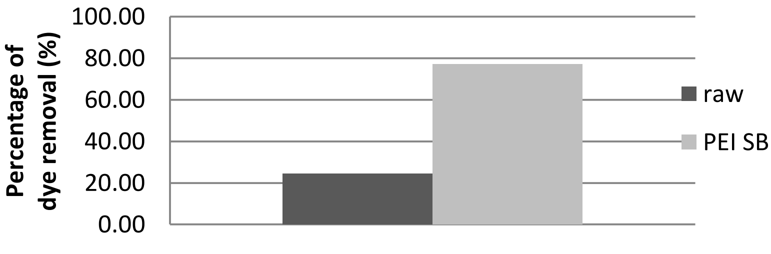

Figure 8: Comparative study between Raw SB and PEI modified SB at optimum condition (contact time = 240 min, adsorbent dosage = 0.1 g/50 mL, dye concentration = 0.05 g/L, pH = 7, temperature = 30 °C)

4. Conclusion

In this study, PEI-modified SB were used to remove MO dye from aqueous solution. The optimum contact time for dye removal is 240 min which the removal was more than 80 %. For adsorbent dosage, the optimum amount is 0.15 g for 50 ml dye solution at pH value 7. The optimum initial dye concentration and temperature for MO dye removal is 0.01 g/L and 30 ºC. This can be concluding that PSB adsorbent is the successful adsorbent with the percentage of dye removal at all parameters effect more than 70 %.

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Reference

Aljebori A.M.K., Alshirifi A.N., 2012, Effect of different parameters on the adsorption of textile dye maxilon blue GRL from aqueous solution by using white marble, Asian Journal of Chemistry 24 (12), 5813–5816.

Amin N.K., 2008, Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sugarcane bagasse pith, Desalination 223, 152–161.

Bazrafshan E., Zarei A.A., Nadi H., Zazouli M.A., 2014, Adsorptive removal of methyl orange and reactive red 198 dyes by Moringa Peregrina ash, Indian Journal of Chemical Technology 21 (2), 105–113.

Basik P., Dan B., Oren R., Penjerapan D., Atas K., Tebu S., Diquarternasi Y., 2009, Removal of Basic Blue 3 and Reactive Orange 16 By Adsorption Onto Quartenized Sugar Cane Bagasse 13 (2), 185–193.

El-Gamal S.M.A., Amin M.S., Ahmed M.A., 2015, Removal of methyl orange and bromophenol blue dyes from aqueous solution using Sorel’s cement nanoparticles, Journal of Environmental Chemical Engineering 3 (3), 1702–1712.

Hamzeh Y., Ashori A., Azadeh E., Abdulkhani A., 2012, Removal of Acid Orange 7 and Remazol Black 5 reactive dyes from aqueous solutions using a novel biosorbent, Materials Science and Engineering: C 32 (6), 1394–1400.

Li H., Sun Z., Zhang L., Tian Y., Cui G., Yan S., 2016, A cost-effective porous carbon derived from pomelo peel for the removal of methyl orange from aqueous solution, Colloids and Surfaces A: Physicochemical and Engineering Aspects 489, 191–199.

Öztekin N., Alemdar A., Güngör N., Erim F.B., 2002, Adsorption of polyethyleneimine from aqueous solutions on bentonite clays, Materials Letters 55 (1-2),73-76.

Sajab M.S., Chia C.H., Zakaria S., Khiew P.S., 2013, Cationic and anionic modifications of oil palm empty fruit bunch fibers for the removal of dyes from aqueous solutions, Bioresource Technology 128, 571–577.

Sharma P., Kaur H., 2011, Sugarcane bagasse for the removal of erythrosin B and methylene blue from aqueous waste, Applied Water Science 1 (3-4), 135–145.

Storck S., Bretinger H., Maier W.F., 1998, Characterization of micro- and mesoporous solids by physisorption methods and pore-size analysis, Applied Catalysis A: General 174 (1-2), 137–146.

Sud D., Mahajan G., Kaur M., 2008, Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – A review, Bioresource Technology 99 (14), 6017–6027.

Tahir H., Sultan M., Akhtar N., Hameed U., Abid T., 2016, Application of natural and modified sugar cane bagasse for the removal of dye from aqueous solution, Journal of Saudi Chemical Society 20 (1), S115–S121.

Tao H.C., Zhang H.R., Li J.B., Ding W.Y., 2015, Biomass based activated carbon obtained from sludge and sugarcane bagasse for removing lead ion from wastewater, Bioresource Technology 192, 611–617.

Thommes M., Kaneko K., Neimark A.V., Olivier J.P., Rodriguez-Reinoso F., Rouquerol J., Sing K.S.W., 2015, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), Pure and Applied Chemistry 87 (9-10), 1051–1069.

Wong S.H.L., Martincigh B.S., 2013, Sugar cane plant fibres: Separation and characterisation, Industrial Crops and Products 47, 1–12.

Zaheer S., Bhatti H.N., Sadaf S., Safa Y., Zia-ur-Rehman M., 2014, Biosorption Characteristics of Sugarcane Bagasse for the Removal of Foron Blue E-Bl Dye From Aqueous Solutions, The Journal of Animal and Plant Sciences 24 (1), 272–279.

Zhang W., Li H., Kan X., Dong L., Yan H., Jiang Z., Cheng R., 2012, Adsorption of anionic dyes from aqueous solutions using chemically modified straw, Bioresource Technology 117, 40–47.