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ADSORPTION OF CATIONIC DYE METHYLENE BLUE FROM AQUEOUS SOLUTIONS ONTO BIOCHAR DERIVED FROM KINNOW (*CITRUS RETICULATA* BLANCO) PEEL

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ABSTRACT

Extensive use of dyes in textile industries results in discharge of high amounts of pollutants in the water bodies. Biochar (BC) derived from Kinnow (*Citrus reticulata* Blanco) peels through pyrolysis was employed as an alternative adsorbent for the removal of methylene blue (MB) dye from aqueous solutions in batch experiment system. The impact of different initial dye concentrations, contact time, adsorbent dose and pyrolysis temperature on adsorption were investigated keeping the solution pH 6 as constant. Adsorption capacity increased when dye concentration was increased from 50 mg/l to 100 mg/l with a decrease in removal efficiency to 37.79%. The biochar showed best removal upto 24 hours indicating equilibrium with a removal efficiency of 96.68%. Of the adsorbent doses, 0.6g was the most suitable one providing maximum adsorptive capacity as well as removal efficiency. The biochar was pyrolysed at 700 °C and 800 °C to study the effect of pyrolysis temperature on MB removal in which biochar having 800 °C as pyrolysis temperature provided higher adsorption of the dye. The present study suggests that the Kinnow peels may be used as an effective low cost adsorbent.

KEYWORDS: Biochar, Methylene blue dye, *Citrus reticulata* Blanco, Pyrolysis, Removal

INTRODUCTION

Due to rapid expansion in the global population, there has been an immense increase in industrialization, particularly the industries related to textiles which use dyes. As an outcome large amount of water is discharged into the environment without any treatment by the industry which eventually leads to pollution in the environment with various dyes (Amin *et al*., 2019). Several industries such as food, tanneries, plastics, cosmetics, paper, printing, pharmaceuticals, and petrochemicals also use a wide range of synthetic dyes. Hence, to eliminate the risk of contamination in different ecosystems, the treatment of effluent containing the toxic residual dyes is very crucial (Vyavahare *et al*., 2018).

Dyes are generally of synthetic origin and are composed of such complex chemical structure which makes them very stable even in the sun exposure and it is very difficult to degrade them biologically, due to which these harmful residues bio-accumulate in the food chain (Kelm *et al*., 2019).

Industrial dyes are classified in three types such as anionic, cationic and non-ionic dyes (Li *et al*., 2018).

Methylene blue (MB) is a heterocyclic, aromatic and also a representative phenothiazine-type monovalent cationic dye (Li *et al*., 2018). The intake of the dye by humans can cause deteriorating health effects such as headache, vomiting, hypertension, fever, mental disorder, jaundice, Heinz body formation, quadriplegia, tissue necrosis and cyanosis (Imron *et al*., 2019).

There are various physiochemical and biological treatment processes for the treatment of effluents discharged from textile industries (Braghiroli *et al*., 2018). Among majority of the treatment processes, adsorption is found to be one of the simple, effective, easy to implement and operate, requiring low energy, and economically effective remediation technique to remove dyes from wastewater or effluents (Shafiq *et al*., 2019; Leite dos Santos *et al*., 2019).

Although there is availability of several commercial adsorbents, but due to their high cost, lack of versatility and limited accessibility the extensive use of these adsorbents is limited. Therefore, utilizing agricultural and industrial wastes which are of low-cost can prove as efficient adsorbents and can be an alternative to commercial adsorbents (Tareq *et al.*, 2019). Agricultural waste such as orange peel (Ali *et al.*, 2016), rice husk (Khan *et al.*, 2010), tea (Shen *et al.*, 2017) etc. have previously been explored as adsorbents for the removal of dyes and heavy metals (Tatarchuk *et al.*, 2019).

In this study, the work on adsorption of MB dye from aqueous solution using biochar derived from kinnow peel has been performed aiming in production of the biochar through pyrolysis at 800 ^{o}C and also consideration and optimization of factors such as initial dye concentration, contact time and amount of biochar has been done to evaluate the potential of biochar for the removal of MB from aqueous solution.

MATERIALS AND METHODS

Preparation of MB dye solution

The dye used in this experiment was methylene blue (MB) ($C_{16}H_{18}N_3SCl$, molar weight 319.85 g/mol, $ë_{max}$ = 668 nm) provided by Central Drug House (P) Ltd.. A stock solution of 1000 mg/l was prepared by dissolving 1g of MB dye in 1l of distilled water. Working solutions of 50 mg/l and 100 mg/l were prepared from the stock solution by diluting in with distilled water. A pH of 6 was adjusted in each of the solutions using 0.1M HCl and 0.1M NaOH accordingly.

Preparation of biochar

The Kinnow peels were collected from a nearby juice centre in Kasna (Greater Noida) and cleaned with distilled water. They were oven dried at 70-80 ^{o}C for about 5 hours or until completely dry. The dried peels were grinded into a mixer grinder to obtain the peel powder. Then the peel powder was pyrolysed into the muffle furnace using the crucibles at 800 ^{o}C for 2.5 hours. After the pyrolysis, the obtained biochar was stored into a beaker and covered with aluminium foil.

Experimental adsorption procedure

After preparing the methylene blue solutions, the biochar was added in each solution and to study the effect of initial dye concentration, contact time and adsorbent dose three set of experiments was carried out accordingly.

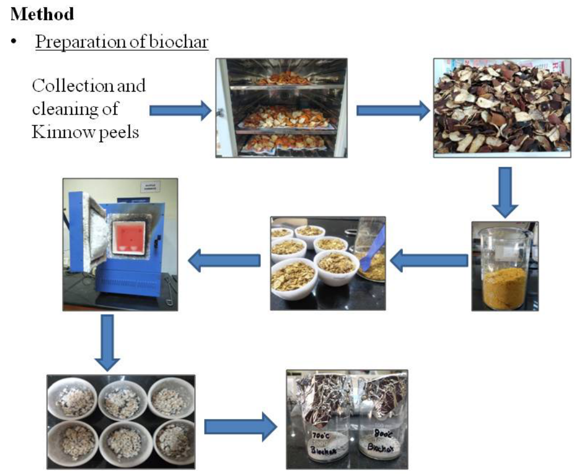

Fig. 1. Preparation of biochar

Variation in initial dye concentrations

Two different initial dye concentrations of 50ppm and 100 ppm were considered. In each batch of experiment, 6 beakers/conical flasks were used in which 3 were filled with 50 ppm solution and the other 3 with 100 ppm solution of 50ml volume.

Variation in adsorbent dose

To study the effect of different adsorbent dose, three amounts were considered i.e., 0.2g, 0.6g and 1g. Hence, 0.2g, 0.6g and 1g of the biochar were added in 50 ppm and 100 ppm solutions each.

Once the biochar addition was completed, all the mixtures were stirred on a hot plate at about 30 ^{o}C for 10 minutes to ensure proper mixing of the adsorbent particles in the solution. After that, the solutions were covered with aluminium foil to prevent photolysis. Along with these, a control was also setup for effective analysis.

Variation in contact time

After addition of biochar, the experiments were carried out for a duration of 36 hours. Frequent sampling was done at time intervals of 6 hours, 12 hours, 24 hours and 36 hours.

To measure the absorbance on decided time intervals, the solutions were pipetted out into eppendorfs and were centrifuged for 5 mins to settle down any adsorbent particles. After centrifugation, the supernatant were transferred into the cuvette and the absorbance was measured at 668 nm using UV-Vis spectrophotometer.

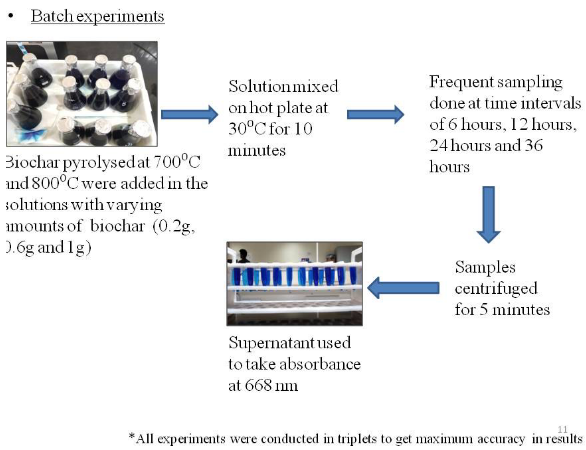

Fig. 2. Batch experiments

To determine the results, the removal efficiency (R, %) using the obtained biochar was measured by the formula:

$$R = \frac{(C_i - C_e) \times 100}{C_i}$$

Also, the amounts of adsorbed MB dye (q_e, mg/g) was measured by the formula:

$$q_e = \frac{(C_i - C_e)\, V}{M}$$

Where, q_e is the adsorption capacity of MB dye (mg/g), C_i and C_e are initial and equilibrium concentrations of MB dye (mg/l) respectively, M is the dry mass of the biochar (g) and V is the volume of the solution (L).

RESULTS AND DISCUSSION

Effect of initial methylene blue dye concentration

The effect of initial MB dye concentration on adsorption by KP (Kinnow peel) biochar was investigated in two different concentrations which were 50 mg/l and 100 mg/l with varying adsorbent doses keeping the dye solution pH 6. As per the change observed in Figure 3 it can be interpreted that the adsorption capacity of KP biochar depends on initial dye concentration. As the dye concentration is increased, adsorption capacity tends to increase i.e., the amount of dye adsorbed on the biochar. The q_e increased from 8.69 mg/g to 17.05 mg/g when the dye concentration increased from 50 mg/l to 100 mg/l. This may be due to the presence of sufficient adsorption sites on the adsorbent which remain unoccupied at low concentration and with the increase in concentration an increased in driving force to overcome mass transfer resistances occurred (Saha, 2010; Ladhe and Patil, 2014; Amin *et al*., 2019). Similar results were reported after working on pomelo (*Citrus grandis*) peel and mosambi (*Citrus sinensis*) bagasse (Hameed *et al*., 2008; Bhatti *et al*., 2012).

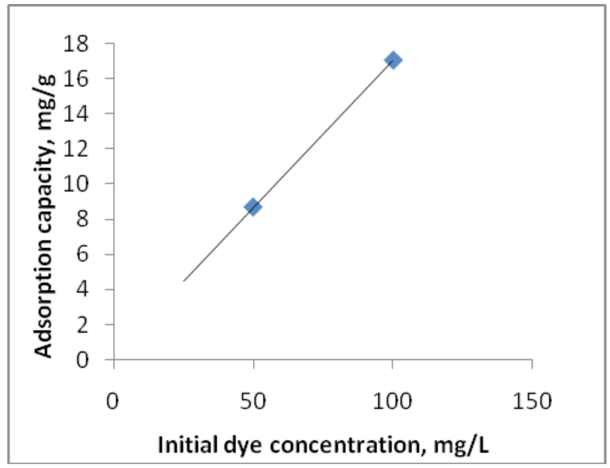

Fig. 3. Effect of initial methylene blue (MB) dye concentration on adsorption capacity

Effect of contact time

Figure 4 shows the effect of contact time on removal efficiency of the prepared KP biochar. A time period of 36 hours was considered for the study of dye removal with frequent sampling being carried out at 6 hours, 12 hours, 24 hours and at 36 hours. It was observed that initially the removal efficiency increased rapidly with increase in contact time but after a contact time of 24 hours, there was only a slight increase in removal efficiency (R%). Removal efficiency increased from 27.61% to 96.43% in duration of 6 hours to 24 hours but at 36 hours removal percent was found to be 96.68%. This can be further explained as initially there are large numbers of binding adsorption sites present at the surface of the adsorbent, but with increase in time the adsorbent surfaces start becoming saturated leading to acquired slow pace in dye removal and a further increase in contact time causes adsorption to reach equilibrium (Saeed *et al*., 2010; Sayðýlý and Güzel, 2016). Therefore, a contact time of 24 hours was found to be the most suitable one as after that the dye removal process attains equilibrium. These results were further supported by the study done on sewage sludge derived biochar for the removal of MB dye (Fan *et al*., 2016).

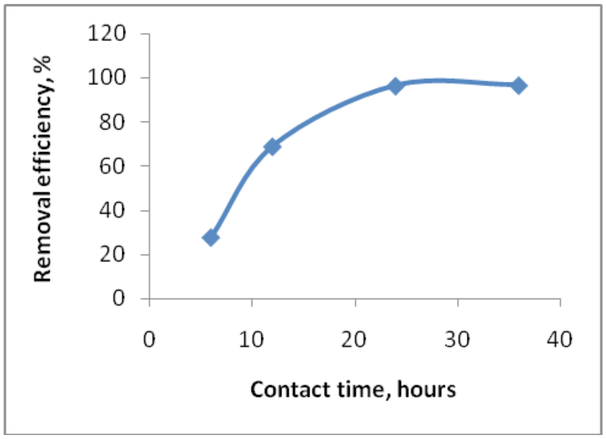

Fig. 4. Effect of contact time on removal efficiency

Effect of adsorbent dose on MB removal

The effect of adsorbent dosage is represented in Figure 5 showing the adsorption capacity of the adsorbent. Varying amounts of adsorbent dose 0.2g, 0.6g and 1g were observed in prepared methylene blue solutions. The adsorption capacity initially increased from 3.26 mg/g to 7.30 mg/g with increase in adsorbent doses from 0.2 g and 0.6g respectively but afterwards decreased to some extent i.e., 5.6 mg/g with increased amount of adsorbent dose of kinnow peel biochar from 0.6 g to 1g. This may be concluded as, there is increase in adsorbent dose the surface area of the adsorbent increases as well as the available sites for adsorption also increases, but on further increase in adsorbent dosage, aggregation of active adsorption sites of biochar particles takes place which in turn reduces the total adsorbent surface area available for methylene blue adsorption (Ahalya *et al*., 2012; Chaukura *et al*., 2017).

Hence, considering the results obtained by studying the effect of different parameters on adsorption of MB dye, the contact time of 24 hours and adsorbent dose of 0.6 g are found to be most suitable and maximum removal or adsorption takes place at these peculiar parameters.

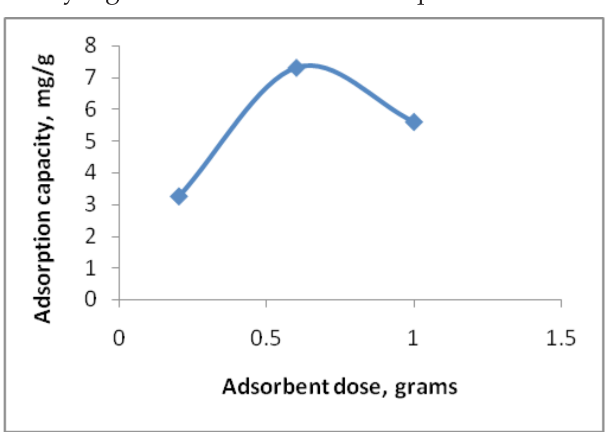

Fig. 5. Effect of adsorbent dose on adsorption capacity

CONCLUSION

The purpose of the present work was to investigate the adsorption potential of Kinnow peel (KP) derived biochar for the adsorption of methylene blue dye from aqueous solution. The obtained results show that they can be used as an alternative low-cost adsorbent for the removal of dyes from aqueous solutions. Kinnow peels were selected for this study due to easy availability as well as to provide the possibility of using such agricultural wastes which otherwise cause environmental and health issues. In this study, the removal efficiency and adsorption capacity of the derived biochar was investigated by varying the factors affecting the process of adsorption or removal such as initial dye concentration, contact time and adsorbent dose. The results obtained show that adsorption capacity increase with increase in initial dye concentration but the removal efficiency decreases. For the contact time, maximum adsorption was found upto 24 hours because after that time duration the adsorption attains equilibrium. Best adsorbent dose was designated to be 0.6g due to highest adsorption being observed.

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