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INTEGRATING ULTRASOUND WITH ACTIVATED CARBON PREPARED FROM MANGOSTEEN FRUIT PEEL FOR REACTIVE BLACK 5 REMOVAL

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Abstract

In this study, the effectiveness of integrating ultrasound with mangosteen fruit peel activated carbon (MFPAC) for the removal of reactive black 5 (RB5) dye was investigated. MFPAC prepared by the potassium carbonate activation method was characterized using BET, SEM and FTIR. The effects of ultrasound power, contact time, pH and adsorbent quantity on the removal of RB5 were examined. Obtained results indicate that the MFPAC has a higher removal efficiency with ultrasound integration and can remove 95% of the dye at neutral pH. It followed pseudo second order kinetics. Integrating ultrasound with sorption was proved to be an efficient method to remove RB5 dye.

Key words: adsorption, Langmuir isotherm, mangosteen fruit peel activated carbon, reactive black 5 dye, ultrasound

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1. Introduction

Water pollution caused by dyes is one of the major threats to the environment. Therefore, removal of textile dyes from aqueous solution has received great attention during recent years. Dye from water medium can be removed by separation (physical and chemical) processes, biological processes or advanced oxidation processes (Khan et al., 2017; Kitinya et al., 2017). The removal of dyes from aqueous solution is not a feasible method, since most of the dyes are non-biodegradable. Various separation methods like adsorption (Fernandez et al., 2014; Khan et al., 2016; Nidheesh et al., 2011; Rauf et al., 2009; Zhou et al., 2011), coagulation (Beltrán-Heredia et al., 2011), combined chemical coagulation/membrane processes (Ellouze et al., 2011; Rodrigues et al., 2017), electrocoagulation (Amani-Ghadim, 2013), etc. and several advanced oxidation processes such as Fenton processes (Kuo, 1992; Saravanan and Sivasankar,

2014), Fenton process coupled with biological processes (Bahmani et al., 2013; Ozkan-Yucel and Gokcay, 2017), peroxicoagulation process (Nidheesh and Gandhimathi, 2014), etc. were applied efficiently for the removal of dyes from water medium. Among these methods, dye removal by the adsorption process got much appreciation due to its less investment in terms of initial development cost, simple design, easy operation, high removal efficiency and no or less generation of toxic substances (Crini, 2006; Khan et al., 2018).

Activated carbon is the well known adsorbent used for the removal of various water contaminants, due to its high porous nature and sorption capacity. Due to the higher cost and regeneration difficulties in commercially available activated carbon, the researchers focused mainly on the preparation of activated carbons from waste materials such as industrial wastes, agricultural wastes, etc. Among the various activation methods, chemical activation offers

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several advantages which involve single step activation, higher yields and better pore structure (Chen et al., 2013). This process involves the impregnation of raw material or charred carbon with activating agent followed by the carbonization process at elevated temperatures (Auta and Hameed, 2011; Li et al., 2011). The activating agents generally used are dehydrating chemical agents like acids, base, etc. Potassium carbonate has been identified as an alternative activating agent for the preparation of activated carbons from various agricultural by-products (Foo and Hameed, 2012).

The application of ultrasound in water and wastewater treatment techniques received great attention in recent days. Improvement in the efficiency of any physical and chemical processes in the presence of ultrasound is mainly due to its cavitation effects. An enhancement of various pollutants sorption in the presence of ultrasound has been reported (Breitbach et al., 2003; Kalidhasan et al., 2012; Midathana and Moholkar, 2009; Schueller and Yang, 2001; Shirsath et al., 2011). The presence of ultrasound increases surface area of adsorbent by forming many micro-cracks on the solid surface and the cleanup of solid particle surfaces (Thompson and Doraiswamy, 1999). The micro-cracks would be facilitated by the microjets produced out of the cavitation process when ultrasound passed into the liquid medium. The enhancement of the pore diffusion coefficient under ultrasonic irradiation results in the increased mass transport of a fluid in the pores of solid particles (Bathen, 2003).

Keeping all in mind, the present work analyzes the dye removal efficiency by integrating ultrasound with activated carbon prepared from the mangosteen fruit peel (MFPAC) waste material. The activated carbon was prepared using potassium carbonate as the chemical activating reagent. Reactive Black 5 (RB5) was used as the model dye to test the sorption efficiency of the prepared adsorbent. This dye has been used in the textile industries for the dyeing of cotton, woolen and nylon fabrics worldwide (Usha et al., 2011). The exposure to this dye may cause allergic reactions to respiratory tract and even worse would cause cancer (Usha et al., 2011). RB5 removal efficiency of the ultrasound integrated MFPAC process was tested at various operational conditions under batch method.

2. Material and methods

2.1. Materials

The chemicals sulphuric acid, potassium carbonate and sodium hydroxide from Merck and the dyestuff from Sigma were used without further purification. Double distilled water is used for preparing all the solutions. Mangosteen Fruit Peels (MFP) were collected from local market. The elemental analysis of MFP was performed using a Perkin Elmer 2400 series II (USA) elemental analyzer. The compositions were found to be, 66.35% C, 1.29%

H, 1.02% N, 0.16% S and 31.18% O indicating the presence of higher amount of carbon in it.

2.2. Preparation of mangosteen fruit peel activated carbon

The collected mangosteen peels were washed with distilled water and dried in a hot air oven at 110°C for 24 hrs for the removal of moisture. After washing and drying, the peels were taken in crucibles and pre-treated with potassium carbonate (K_2CO_3) in a mass ratio of 2:1. Small amount of de-ionized water was added to each crucible and the samples were soaked in potassium carbonate solution. The samples were again dried at 110°C in hot air oven for 24 hrs. After pre-treatment, the samples were carbonized and activated in a muffle furnace at 700°C for 2 hrs in an inert atmosphere. Nitrogen gas at a flow rate of 150 cm^3/min was used for the maintenance of inert atmosphere in the muffle furnace where the heating rate was 10°C/min. The carbonized/treated samples were washed with dilute sulfuric acid (0.1M) and distilled water until the pH of the samples becomes neutral, which was pH 7. The activated carbon sample was dried in hot air oven at 110°C for 24 hrs. After drying, the activated carbon was ground to powder form using mortar and pestle.

2.3. Characterization of mangosteen fruit peel activated carbon

Mangosteen fruit peel and the prepared MFPAC were characterized by different methods viz. Thermogravimetric analysis (TGA) using TA instruments (SDT Q600 V20.9 Build 20), Fourier transform infrared spectroscopy (FTIR) using Spectrum Two FT-IR Spectroscopy, Brunauer Emmett Teller isotherm based analysis (BET) using Micromeritics (ASAP 2020 V3.04 H) and scanning electron microscopy analysis (SEM) using JEOL (JSM-6460 LV) to analyze the physical and chemical characteristics.

2.4. Ultrasound integrated adsorption studies

Ultrasound integrated adsorption experiments were carried out in batch mode. 100 mL of 10 mg/L RB5 solution was used in a glass conical flask immersed in an ultrasound bath to a certain level (i.e.40mm from the bottom of the inner tank) which was maintained for all the experiments. The dye removal experiments were done using an ultrasound bath (Elma Transsonics Inc., Model: T490DH) made of stainless steel with an operating frequency of 40 kHz, variable ultrasound power (from 22 to 132 W in scale of 22) and maximum tank volume of 2.75 L. The conical flask was positioned in the middle of the ultrasound and the level of water filled (2/3rd) in the ultrasound bath were maintained constant for all the experimental studies. The initial solution pH was adjusted using 0.5 N H_2SO_4 and 0.5 N NaOH. pH meter (YSI Professional Plus, USA) was used for

measuring pH of the solution. The known amount of adsorbent was added into this solution and the sonication was carried out up to a contact time of 60 min for all the experimental study unless otherwise mentioned. During sonication, samples were withdrawn at regular interval and centrifuged for 3 min to separate the adsorbent from the liquid. Then, the residual concentration of RB5 was measured using UV-Visible Spectrophotometer (JASCO, Japan) which shows the peak absorbance at 597 nm.

3. Results and discussion

3.1. TGA analysis of MFP

The TGA curve of Mangosteen Fruit peel (MFP) is shown in Fig.1. The weight loss at the initial stages (temperature from 23°C to 100°C) is mainly due to the evaporation of adsorbed water on the MFP. After that the MFP is thermally stable upto a temperature of 170°C. Then, sudden decrease in the MFP weight loss was observed upto 350°C and the decrease in weight loss continued slowly. This sudden decrease in weight indicates the removal of highly volatile organic matter presented in the MFP. The gradual decrease in weight after 350°C may be due to the thermal decomposition of polymers present in the MFP. 31.2% of MFP was remained after 1000°C which indicates the higher concentration of carbon in MFP and it will be a good source of activated carbon.

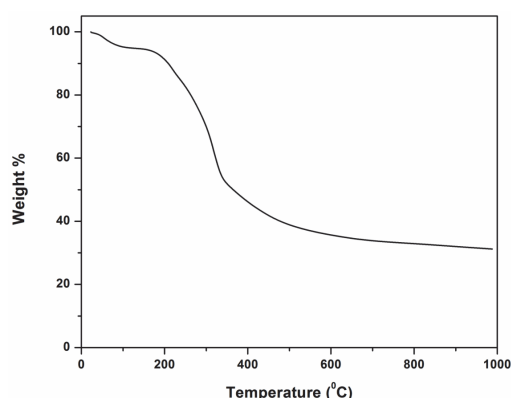
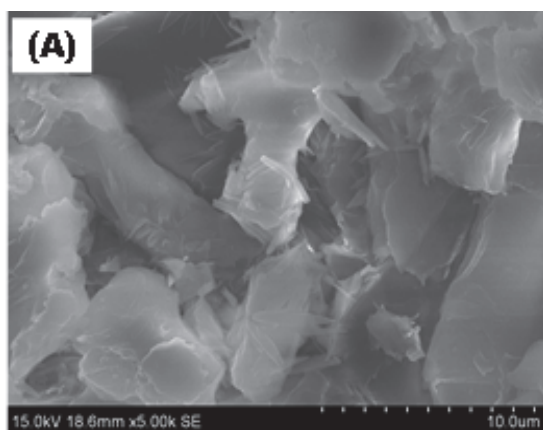


Fig. 1. TGA curve of MFP



3.2. SEM analysis of MFP and MFPAC

The SEM images of MFP and MFPAC are shown in Fig. 2. The MFP is having a dense and uneven morphology. The pores present on the surface MFP are very less. In contrary to this, the pores of MFP increased significantly after the activation process. This is mainly due to the sudden burst and thermal expansion of the MFP material during the pyrolysis process (Ahmad and Alrozi, 2010). These voids are distributed homogeneously over the surface of MFPAC and all together MFPAC morphology resembles to a honey bee nest. This revealed that the activation process using potassium carbonate and carbonization is an effective method for the production of activated carbons with homogeneously distributed pores. The size and shape of these pores are identical and indicates that the MFPAC can adsorb a variety of pollutants.

3.3. BET analysis of MFPAC

Qualitative information on adsorption mechanism and pore structure of prepared MFPAC was obtained from the nitrogen adsorption and desorption isotherm curve. The nitrogen adsorption desorption curve of MFPAC is shown in Fig. 3. The obtained curve resembles a combination of type I and type II isotherms as per IUPAC recommendations (Foo and Hameed, 2012). This indicates that the prepared material is a combination of microporous and mesoporous structure. The detailed pore size characteristics of MFPAC are given in Table 1. The pores of adsorbents are classified into micropore ($d < 2$ nm), mesopore ($d = 2-50$ nm) and macropore ($d > 50$ nm) based on IUPAC-pore dimensions (Foo and Hameed, 2012). In the present study, the average pore size of MFPAC is 2.34 nm, indicates that the pores fell in to the mesopore region. But as per the data provided in Table 1, mesopore volume is substantially lesser than that of micropore volume. This indicates that the material has more micropore than mesopore, which is important for an adsorbent. The insert picture in the Fig. 3 shows the cumulative pore volume distribution along with pore width which again supports the claim microporous nature of the MFPAC.

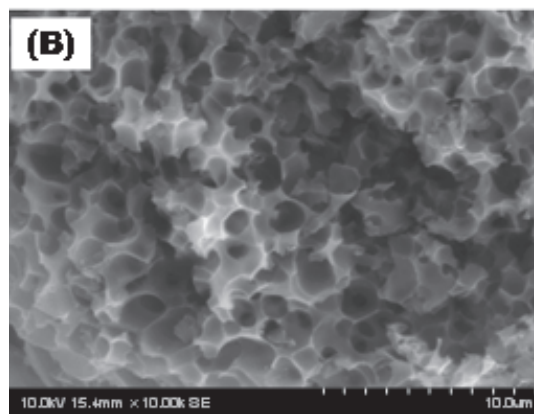


Fig. 2. SEM images of (a) MFP and (b) MFPAC

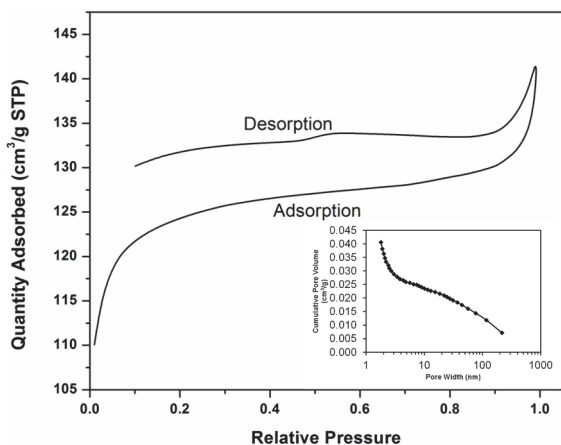


Fig. 3. Nitrogen adsorption-desorption curve of MFPAC

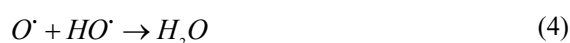
Table 1. Porosity structure of MFPAC

No.	Properties	Values
1	BET surface area	377.23 m ² /g
2	Micropore surface area	329.81 m ² /g
3	External surface area	47.41 m ² /g
4	Total pore volume	0.22 cm ³ /g
5	Micropore volume	0.17 cm ³ /g
6	Mesopore volume	0.05 cm ³ /g
7	Average pore size	2.34 m

3.4. Effect of sonication power and the addition of MFPAC

Initially, sorption of RB5 only in the presence of MFPAC was tested and only 19% of dye removal was observed. To enhance process, simple ultrasound treatment of 10 mg/L RB5 solution was carried out at various sonication powers ranging from 22 to 132 W to study its effect on dye removal. The RB5 removal increased with the increase in sonication power (Fig. 4) and attained a maximum removal of 20% for 132 W US power.

The removal of dyes only in the presence of US is mainly by the degradation of RB5 by the oxidants (predominantly $\bullet H$ and $\bullet OH$ radicals) produced from the acoustic cavitation phenomenon. Hydroxylation and pyrolysis are the main two mechanisms for the sonochemical degradation of organic pollutants (Sivasankar and Moholkar, 2010). But in this situation, hydroxylation is the main mechanism for the removal of RB5 with the irradiation of US. With the addition of US in the aqueous solution, micro-bubble formation occurs in the system. These micro-bubble collapses within a very small fraction of time and results in the generation of very high temperature and pressure conditions inside the bubble. This leads to the formation of free radicals as in the Eqs. (1-8) (Gogate and Pandit, 2004a; Gogate and Pandit, 2004b). The increased removal with an increase in sonication power is mainly due to the increase in free radical formation in the aqueous media.



It can also be seen from the Fig. 4 that the induction of MFPAC (1 g/L) into the solution increased the dye removal efficiency of the sonication process. In all the sonication powers, a significant increase in dye removal efficiency with the addition of adsorbent was noticed when compared with simple ultrasound treatment alone. Due to the cavitation process local turbulence, intense circulation currents (acoustic streaming), high shear stress in the vicinity of the bubble and the formation of micro-jets near the solid surface etc. also occurs in the aqueous medium (Sutkar et al., 2010). This leads to the uniform mixing of solution and higher interaction between adsorbent and dye which causes the increased chances of sorption process. It is reported that for a batch adsorption process, ultrasound acts like a mixer improving the mass transfer coefficient through cavitation and acoustic streaming (Schueller and Yang, 2001).

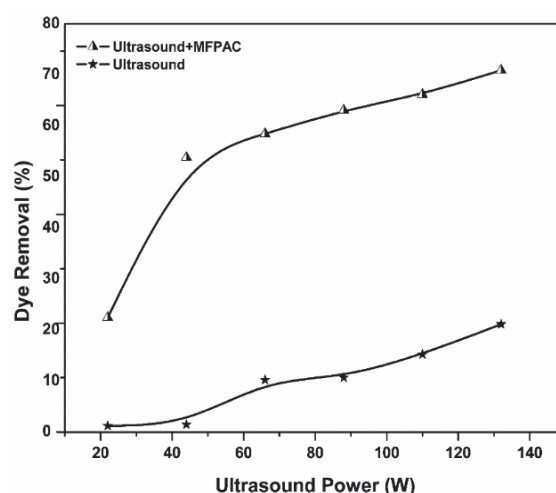


Fig. 4. Effect of sonication power and MFPAC addition on RB5 removal (Experimental conditions: Solution pH 7; RB5 concentration of 10 mg/L; MFPAC concentration of 1 g/L)

Also, due to micro-turbulence created by cavitation, the liquid film thickness surrounding the adsorbent decreases and results in an enhancement in the diffusion rate of dye molecules from the bulk phase to liquid boundary layer around the adsorbent surface

(Nidheesh et al., 2011; Patil, et al., 2011). Since the temperature of the solution partially increases by the cavitation process with ultrasound power, the rate of sorption of dye on MFPAC also increases (Nidheesh et al., 2011). This indicates that the sorption of RB5 on MFPAC is an endothermic process. The results obtained indicate that the combination of US and adsorbent with higher sonication power (i.e. ~71% removal for 132 W) has an enhanced power to remove the dyes from aqueous solution.

3.5. Effect of solution pH

Effect of solution pH on ultrasound (US) integrated sorption of RB5 on MFPAC (1 g/L) with minimum ultrasound power of 22 W is shown in the Fig. 5. From the figure, it can be observed that the sorption of dye on MFPAC decreased with increase in solution pH from 2 to 7 and further increase in pH increased the dye removal efficiency of MFPAC. The maximum dye removal of 88% was observed at solution pH 2.

The enhancement in dye removal with a decrease in pH is mainly due to the increased production of free radicals at lower pH values. Also, the oxidation capacity of hydroxyl radicals produced in acidic conditions is higher than that at alkaline conditions (Mishra and Gogate, 2010). For the sonochemical removal of organic pollutants, various researchers reported the optimal acidic conditions. Khokhawala and Gogate (2010) observed pH 2 as the favourable condition for the mineralization of phenol from the aqueous solution. Shriwas and Gogate (2011) reported 2.5 as the optimal pH for the efficient degradation of methyl parathion in aqueous solutions. Similarly, Mishra and Gogate (2010, 2011) observed the same optimal pH for the degradation of Rhodamine B.

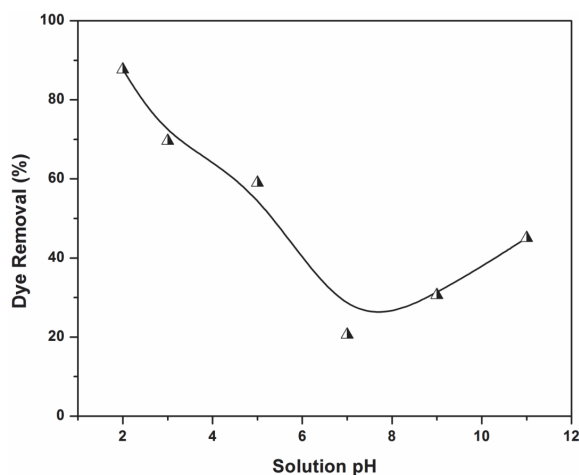


Fig. 5. Effect of solution pH on RB5 removal by US assisted adsorption process (Experimental Conditions: RB5 concentration of 10 mg/L; Sonication power of 22 W; MFPAC concentration of 1 g/L)

A significant removal of RB5 in the alkaline conditions was also observed and the removal was increased with the increase in solution pH from 7. At these conditions, the competitive reaction for the effective sorption on MFPAC active site occurs between the hydroxyl ions and negatively charged RB5 molecules. Since, the size of the RB5 is higher than that of hydroxyl ions, more dyes are sorbed on the adsorbent surface. Also, a repulsive force occurs between hydroxyl ions and RB5 in the solution at alkaline conditions. These repulsive forces increase with solution pH and favors more sorption of dyes by MFPAC.

3.6. Effect of contact time and adsorption kinetics

The effect of contact time on the ultrasound integrated sorption of RB5 by MFPAC was carried out to find the equilibrium time required for the effective sorption and the results obtained is shown in Fig. 6. From the figure, it can be seen that rate of RB5 uptake by MFPAC was very high at the initial stages of sorption process. This rapid uptake at the initial stages of sorption process is mainly due to the availability of higher amount of active sites responsible for the sorption process. Further increase in contact time decreased the uptake rate and reached equilibrium after 30 min of contact time. After this equilibrium, the amount of RB5 desorbed from MFPAC is in dynamic equilibrium with that of adsorbed concentration. Pseudo first and second order kinetics were applied to find the rate of sorption of RB5 on MFPAC. The pseudo first and second order kinetic equations are given as Eqs (9-10):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (9)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t , respectively (mg/g), k_1 is the rate constant of pseudo first-order adsorption (1/min) and k_2 is the rate constant of pseudo second-order adsorption (g/mg/min).

The values of kinetics constants calculated are given in Table 2. In both kinetic models, the value of correlation coefficient is very high. But, the model predicted and experimental values of q_e are almost same for pseudo second order model, indicates that the ultrasound integrated sorption of RB5 on MFPAC follows pseudo second order kinetics. This is also observed in Fig. 6 that, the pseudo second order model predicted values of remaining dye concentration are in good agreement with that of experimental values. But a deviation for pseudo first order model predicted values from the experimental data was observed.

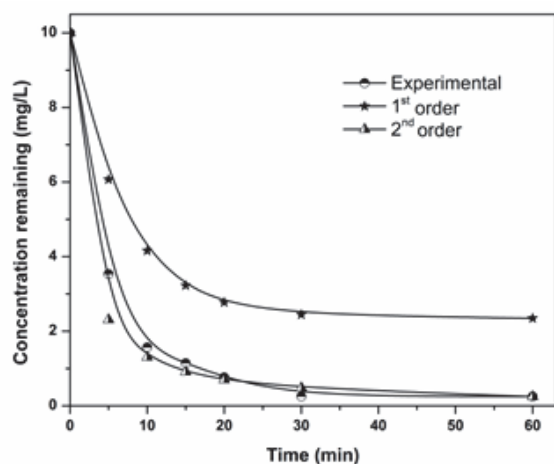


Fig. 6. Rate of RB5 reduction on MFPAC and its comparison with pseudo first and second order kinetics results

Table 2. Kinetic parameters for the ultrasound integrated adsorptive removal of RB5 by MFPAC

Pseudo first order kinetic model		Pseudo second order kinetic model	
k_1 (1/min)	R^2	k_2 (g/mg/min)	R^2
0.144	0.96	0.02	0.99

3.7. Effect of adsorbent quantity

Since the amount of active sites responsible for the sorption of dyes depends more on the amount of adsorbent, MFPAC concentration is an important parameter controlling the sorption process. The effect of adsorbent quantity on the sorption of RB5 in the presence of US with minimal ultrasound power of 22 W and at neutral pH condition is shown in Fig. 7. From the figure, it can be seen that the MFPAC concentration has a significant effect on the sorption of RB5. The dye removal efficiency of US assisted adsorption process increased with the increase in adsorbent concentration. For example, the dye removal percentages at MFPAC concentrations of 1 g/L and 3 g/L were observed as 26 and 95% respectively. This increase in dye removal with an increase in adsorbent quantity is mainly due to the increased amount of active sites. Therefore, 3 g/L of MFPAC was considered as the optimal adsorbent concentration for the sorption of RB5.

Overall, it could be concluded that when comparing the removal efficiency of RB5 dye by activated carbon prepared from mangosteen fruit peel with the reported literature (Osma et al., 2007; Xue et al., 2009; Tanyildizi, 2011; Samarghandy et al., 2011; Heibati et al., 2014; Shirzad-Siboni et al., 2014) of various activated carbon prepared from different materials, all the reported adsorbents have better maximum removal percentage at acidic pH, whereas the present study had demonstrated that with neutral pH and integrating ultrasound at lower ultrasound power with adsorbents would yield higher removal percentage

than simple adsorption for the condition studied.

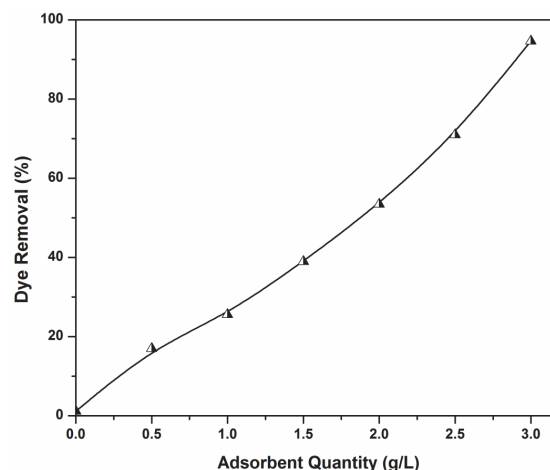


Fig. 7. Effect of adsorbent quantity on the sorption of RB5 (Experimental Conditions: Solution pH 7; RB5 concentration of 10 mg/L; Sonication power of 22 W)

3.8. FTIR Analysis

FTIR analysis was carried out for MFP, MFPAC, RB5 and for MFPAC sample after it had undergone ultrasound assisted adsorption of RB5 and the results obtained are shown in Fig. 8. From the figure, it can be seen that many adsorption bands in MFP have disappeared by the activation process. This indicates the higher amount of volatile organic contents in the MFP and confirms the results obtained from the TGA analysis. The peaks of MFP were observed at 3406, 2925, 1718, 1614, 1450, 1383, 1283, 1058 cm^{-1} and are corresponding to surface hydroxyl groups, asymmetric stretching of C-H, N-CH₃, NH₂, asymmetric bending of CH₃, N-CH₃ stretching, C-N, C-C or C-O stretching respectively. In the case of MFPAC, the peaks were observed at 3741, 3425, 2919, 2853, 1566 and 1052 cm^{-1} . These peaks are corresponding to silanol groups, surface hydroxyl groups, C-H stretch, CH₂ stretching, asymmetric N-H deformation and C-C or C-O stretching respectively. A sharp increase in most of the band transmittance values of MFP was observed after the activation process. At the same time, a sharp decrease in the transmittance value at 670 cm^{-1} was also observed with the activation of MFP. This peak is mainly due to CO₃²⁻ and the decrease in transmittance value indicates the increased concentration of carbonates after the activation process.

Comparing the peaks of RB5, MFPAC and RB5 adsorbed MFPAC, it can be seen that the sorption of RB5 was occurred effectively on the surface of MFPAC. It is clearly indicated by the decrease in transmittance values at the 2853 and 2919 cm^{-1} bands. At the same time, the transmittance value at 3425 and 1052 cm^{-1} decreased after the sorption process. This indicates that the surface hydroxyl groups and C-C or C-O groups on MFPAC are responsible for the sorption of RB5 on MFPAC.

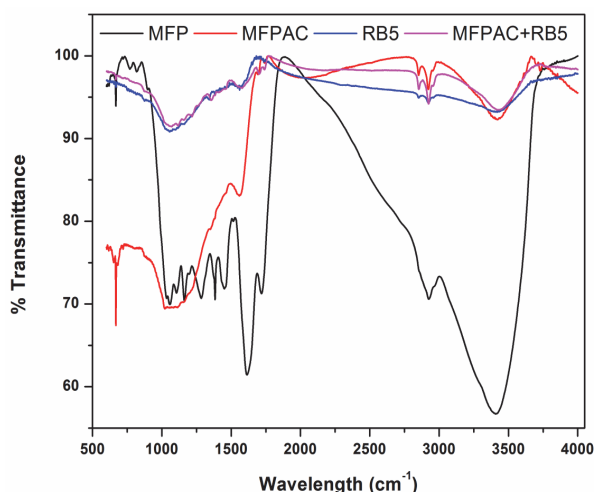


Fig. 8. FTIR spectra of MFP, MFPAC, RB5 and RB5 adsorbed MFPAC

4. Conclusions

In the present study activated carbon from the mangosteen fruit peel waste material was prepared by chemical activation method and were characterized. The prepared material was found to be highly porous and had a higher efficiency for the removal of RB5 dye from aqueous solution when integrated with ultrasound. The equilibrium time was found to be 30 min and almost 95% of dye was sorbed by MFPAC at a low ultrasound power of 22 W, 3 g/L MFPAC and neutral pH conditions.

The ultrasound assisted sorption of RB5 dye on MFPAC follows pseudo second order kinetics. The obtained results indicate that integrating ultrasound with sorption would provide an efficient removal of dyes from aqueous solution.

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