*Desalination and Water Treatment*
www.deswater.com
doi: 10.1080/19443994.2014.967727

56 (2015) 2872–2878
December

Taylor & Francis
Taylor & Francis Group

# Preparation of adsorbent using sugarcane bagasse by chemical treatment for the adsorption of methylene blue

Vrushali N. Gardare, Shivaraj Yadav, Devchand N. Avhad, Virendra K. Rathod*

*Department of Chemical Engineering, Institute of Chemical Technology, Matunga (E), Mumbai 400019, India, Tel. +91 22 33612020; Fax: +91 22 33611020; email: vk.rathod@ictmumbai.edu.in (V.K. Rathod)*

Received 22 January 2014; Accepted 5 September 2014

ABSTRACT

The main emphasis of the present study was to prepare a low-cost adsorbent using sugarcane bagasse for the adsorption of methylene blue. Chemical activation using di-potassium hydrogen phosphate ($K_2HPO_4$) was employed for the preparation of activated carbon by one-factor-at-a time methodology using batch operation. Different process parameters such as $K_2HPO_4$ concentration, impregnation time, temperature, and impregnation ratio were optimized for the chemical treatment of bagasse. The optimized protocol yielded 136.84 mg/g binding capacity in the activated carbon composed of 2 M $K_2HPO_4$ solution-treatedbagasse powder (treated for 6 h with an impregnation ratio of 0.0125 at 30°C temperature); while sugarcane bagasse without any pretreatment was found to have a binding capacity of 125.06 mg/g. The methylene blue adsorption capacity of the chemically treated adsorbent was compared to the commercial activated carbon. Reduction in the characteristic peak intensities of IR spectroscopy and scanning electron microscopy studies indicates structural changes in chemically activated bagasse powder. Prepared adsorbent has tremendous potential for adsorption of harmful dyes and chemicals from polluted water system.

*Keywords:* Sugarcane bagasse; Adsorption; Chemical activation; $K_2HPO_4$; Methylene blue

## 1. Introduction

The textile industry is a major producer of waste water effluents containing dyes, surfactants, salts, and alkalis along with other hazardous chemicals. Waste water from the industries cannot be directly released to the aquatic system as it may reduce the photosynthetic activity of aquatic life and also may be toxic to certain forms of the aquatic life [1]. Various effluent treatment processes were developed to encounter health hazards such as chemical precipitation, solvent extraction, adsorption, ion exchange, and reverse osmosis [2]. Among these processes, activated carbon adsorption seems to be one of the efficient technologies. Activated carbon is the most commonly used adsorbent as it has a high adsorption capacity owing to its high surface area and microporous structure but has a poor regeneration capacity and is expensive [1]. Hence, in order to make the adsorption process environment friendly and economically feasible, researchers have suggested the use of biosorbents as an alternative to activated carbon, which include various agricultural wastes and raw plant materials such as peanut husks [3–5], rice husk [2,6,7], coconut husk [8], almond shells [9], coir pith [10], and sawdust [11]. For the enhancement of adsorption capacity, biosorbent

*Corresponding author.

was given a chemical treatment (impregnated with acid, base, or salts). During the chemical treatment, agricultural waste was impregnated with acid, base, or salt by stirring. Chemical treatment replaces the lignocellulosic functional groups such as the –OH, phenolic groups by the more negatively charged groups of the acid, base, or salt, thereby favoring an increase in the adsorption capacity. In the present study, the impregnation is carried out using stirring operation where the material along with the chemical activator is kept for stirring in a batch reactor. Due to stirring, the intra-particle diffusion rate increases and the solute particles get attached to the lignocellulosic functional groups which impart new properties to the adsorbent, thereby increasing its adsorption capacity. Methylene blue being a cationic dye replaces the hydroxyl and phenolic groups with acidic phosphate groups and favors dye adsorption as it forms complexes with the negative acid groups.

In the present study, sugarcane bagasse was studied as an adsorbent using chemical treatment. Sugarcane bagasse is the fiber material left after extraction of juice from the sugarcane stalks. Previously, low-cost adsorbents such as peanut husk [3–5], rice husk [6,7], coconut husk [8], almond shells [9], coir pith [10], saw dust [11], and oil palm fiber [12] have been used for the removal of dyes either in their native form or for chemical or physical activation, or for both. Sugarcane bagasse has been previously used for the adsorption of various dyes without any chemical activation [13–15]. Sugarcane bagasse was explored as an adsorbent in its native form, pretreatment with different chemicals, and immobilized form [16,17], and it was reported that maximum dye adsorption was shown by the pretreated form of bagasse. The rice husk, chemically pretreated with $K_2HPO_4$, was used for the adsorption of cadmium [2]. Here, sugarcane bagasse is explored as an adsorbent for the adsorption of methylene blue dye, where the bagasse is impregnated with $K_2HPO_4$ solution. The main aim was to carry out an optimization for the chemical treatment of adsorbent preparation. Process parameters such as the concentration of $K_2HPO_4$ solution, impregnation time, temperature, and impregnation ratio were chosen as the crucial factors affecting the adsorption capacity of sugarcane bagasse. The optimization was carried out in a stepwise manner, where a single parameter was varied every time keeping the other parameters at a constant value in a batch operation. The prepared adsorbent was tested using the methylene blue assay, where methylene blue solution was adsorbed onto the prepared adsorbents and the absorbance of solutions before and after adsorption was measured using a UV–visible spectrophotometer.

## 2. Materials and methods

Sugarcane bagasse was procured from local market, Mumbai, India. Dipotassium phosphate salt, standard activated carbon, and other analytical grade chemicals were procured from S.D. Fine chemicals, Mumbai, India.

### 2.1. Adsorbent preparation and experimentation

Sugarcane bagasse was dried and stored in an air-tight bag. The bagasse was sieved using ASTM standard sieve (a particle size of 212 μm). In order to carry out chemical activation, 5 g bagasse powder was treated with different concentrations of 100 mL $K_2HPO_4$ solutions (0.5–3 M) keeping the impregnation time (24 h), impregnation ratio (0.05), and temperature (30˚C) at a constant value in a baffled reactor of 200 mL volume, with a diameter of 4 cm and a height of 16 cm in a controlled water bath with an impeller speed of 300 rpm. Treated solutions were filtered and the adsorbent was dried and stored under ambient conditions. The prepared samples were analyzed by methylene blue assay using UV–visible spectrophotometer and optimum $K_2HPO_4$ concentration was determined. After optimization of $K_2HPO_4$ concentration, optimization of impregnation time, impregnation ratio, and temperature were carried out in a similar manner by one-factor-at-a time method. The amount of bagasse taken was changed accordingly during the optimization of impregnation ratio.

### 2.2. Methylene blue assay

0.1 g of each sample was treated with 30 mL of 750 ppm of methylene blue solution and the solution was kept for stirring in an orbital shaker with a rotation speed of 180 rpm for 2 h. The absorbance of the clear solutions was measured using UV–visible spectrophotometer (Spectroscan UV 2700, Double Beam UV–visible Spectrophotometer, Chemito, India) at a wavelength of 665 nm. The adsorption capacity was found using the following equation :

$$q_e = (C_i - C_e) \times \frac{V}{m} \tag{1}$$

where $q_e$ is the adsorption capacity (mg/g), $C_i$ is the concentration of the stock solution, $C_e$ is the concentration of the solution after adsorption, $V$ is the volume of solution, and $m$ is the mass of adsorbent.

### 2.3. Statistical analysis

Statistical analysis was performed using one-way ANOVA. Experimental data were processed by Graph pad prism 5.0 software (USA) and $p$-value less than 0.05 was considered to be statistically significant.

### 2.4. Characterization of sugarcane bagasse powder

Normal and chemically activated sugarcane bagasse powder was analyzed by infrared spectroscopy for the identification of functional group changes. Also, surface morphology of the normal and chemically activated sugarcane bagasse powder was studied using the scanning electron microscopy (SEM) technique (JEOLJSM6380 LA scanning electron microscope).

## 3. Results and discussion

### 3.1. Effect of concentration of $K_2HPO_4$

The effect of concentration of $K_2HPO_4$ on the adsorption capacity of chemically activated sugarcane bagasse was studied by varying its concentration in the range of 0.5–3 M. Fig. 1 reveals that the adsorption capacity increases as the concentration of $K_2HPO_4$ increases initially up to 2 M, but beyond 2 M, there was a decrease in the adsorption capacity. The maximum adsorption capacity at 2 M concentration was 130.6 mg/g ($p$ value <0.05). Initially, the phosphate groups replaced the lignocellulosic functional groups, thereby increasing the availability of negatively charged surface on the adsorbent which favored an increase in the adsorption capacity. A further increase in the $K_2HPO_4$ concentration was found to erode the adsorbent surface due to excessive phosphate ions, leading to a decrease in the adsorbent surface area and a reduced adsorption capacity.

### 3.2. Effect of impregnation time

Impregnation time is one of the important parameters as it decides the interaction time of $K_2HPO_4$ with bagasse and thus the chemical activation. Experiments were performed for different impregnation time and the results are reported in Fig. 2. The adsorption capacity was found to increase with the impregnation time till 6 h and further increase in time gives marginal variation in the adsorption. The addition of phosphate ions to bagasse was found to increase the adsorption capacity. As time progressed, phosphate ions were attached to all the sites and thereafter, a slight increase was seen in the adsorption capacity which was an indication that all the sites were slowly replaced by phosphate ions leading to a constant adsorption capacity. The adsorption capacity increased rapidly up to 6 h, with a slight increase in the adsorption capacity at further impregnation (12 and 24 h) ($p$ value <0.05). An increased impregnation time had provided a better contact time but as the chemical activation was found to be complete at 6 h, with no further significant increase in the adsorption capacity

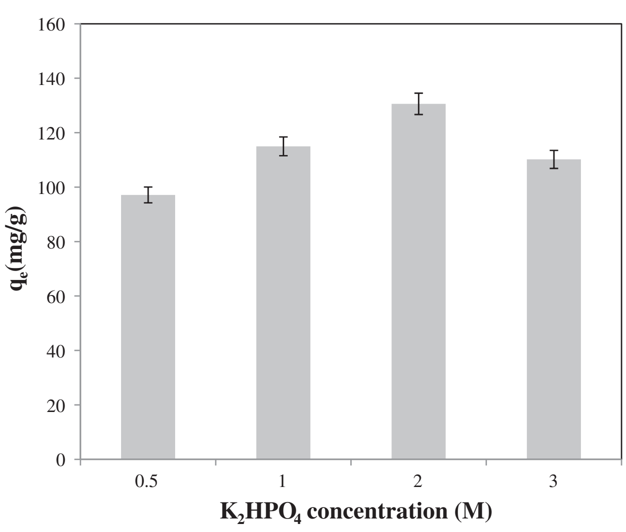


Fig. 1. Effect of $K_2HPO_4$ concentration on the adsorption of methylene blue (impregnation time: 24 h, impregnation ratio: 0.05, and temperature: 30˚C).

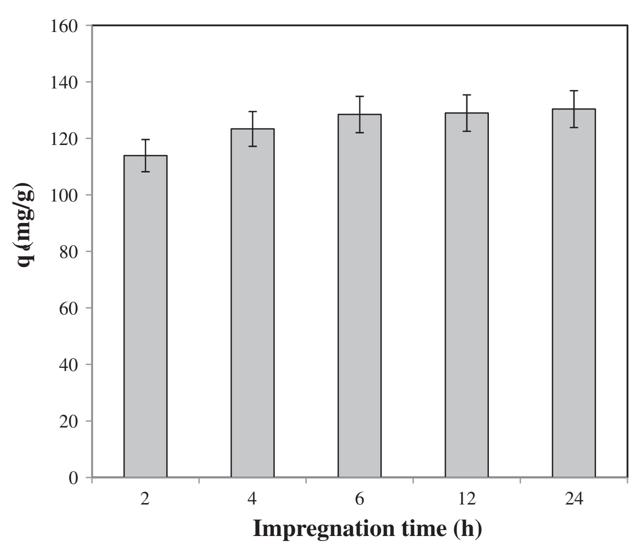


Fig. 2. Effect of impregnation time on the adsorption of methylene blue ($K_2HPO_4$ concentration: 2 M, impregnation ratio: 0.05, and temperature: 30˚C).

at higher impregnation time, the 6-h impregnation time was considered as the optimum for further studies.

### 3.3. Effect of temperature

Temperature decides the transfer of phosphate ions through the bagasse pores as it affects the viscosity of the solution. Thus, effect of temperature was determined at different temperatures, i.e. 10, 20, 30, 40, and 50˚C and results are depicted in Fig. 3. Temperature at 30˚C was found to be the best for chemical activation during the adsorbent process. The adsorption capacity ($q_e$) at 40˚C (130.03 mg/g) was slightly higher than at 30˚C (128.45 mg/g), but the chemical activation at a higher temperature would require more energy and hence the optimum temperature was considered to be 30˚C ($p$ value <0.05). Low temperature was not enough for the chemical activation to take place as viscosity of solution increases and it becomes difficult for the phosphate ions to diffuse into the bagasse. However, high temperature may lead to the distortion of porous structure of sugarcane bagasse which affects the binding site and leads to a decrease in the adsorption capacity.

### 3.4. Effect of impregnation ratio

Impregnation ratio was found to be an important parameter during the chemical activation of adsorbent as it influenced the adsorption capacity. It is the ratio of the amount of bagasse powder used to the volume of $K_2HPO_4$ solution (g/mL). The ratio varied for

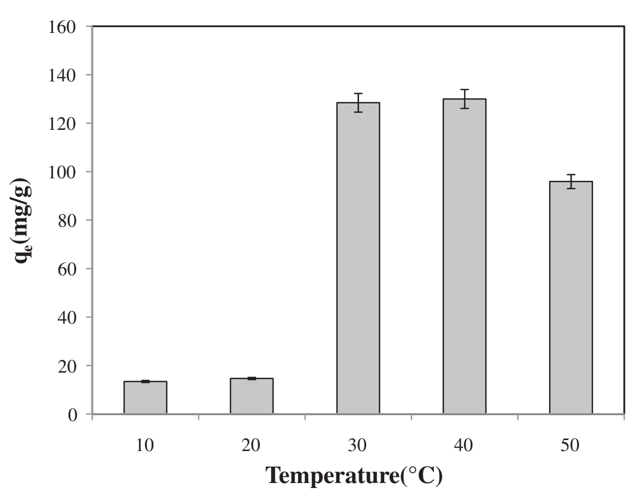


Fig. 3. Effect of temperature on the adsorption of methylene blue ($K_2HPO_4$ concentration: 2 M, impregnation time: 6 h, and impregnation ratio: 0.05).

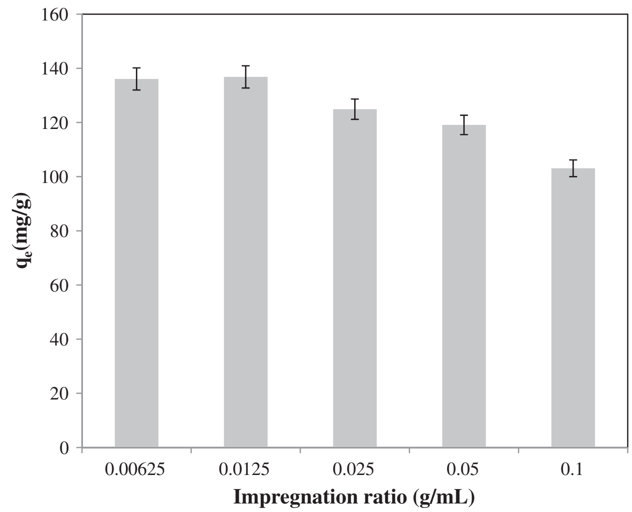


Fig. 4. Effect of different impregnation ratio on the adsorption of methylene blue ($K_2HPO_4$ concentration: 2 M, impregnation time: 6 h, and temperature: 30˚C).

$K_2HPO_4$ concentration of 2 M and the $q_e$ was found to be 136.84 mg/g for an impregnation ratio of 0.0125 ($p$ value <0.05). A lower impregnation ratio destroyed the porous structure of the adsorbent surface due to the higher concentration of phosphate ions as compared to the amount of bagasse taken, while a higher impregnation ratio led to an insufficient contact between the bagasse and $K_2HPO_4$ solution (Fig. 4)

Adsorption capacity of the prepared adsorbent at optimum conditions was 136.84 mg/g, while standard activated carbon had 236 mg/g. After comparing the adsorption capacity, it seems that there are chances for improvement in the adsorption capacity of the bagasse powder. The adsorption capacity of methylene blue by various other adsorbents has been mentioned in Table 1, and it shows that chemically treated bagasse with an adsorption capacity of 136.84 mg/g and natural bagasse with an adsorption capacity of 125.06 mg/g have a good scope to be used as an adsorbent ($p$ value <0.05).

### 3.5. Characterization of chemically activated bagasse powder

IR spectroscopy results of normal and chemically activated powder are shown in Fig. 5(A) and (B). The difference indicated that the structure of bagasse was changed after $K_2HPO_4$ treatment, and the changes were both intra- and inter-molecular. The intramolecular changes were represented by the decreases in functional group contents. Each glucose group of sugarcane bagasse has three alcoholic hydroxyl

Table 1
Comparison of adsorption capacity of various adsorbent for methylene blue

| Sr. No. | Adsorbent name | MB adsorption capacity (mg/g) | Reference |
|---|---|---|---|
| 1. | Orange peel | 18.6 | [18] |
| 2. | Banana peel | 20.8 | [18] |
| 3. | Rice husk | 28 | [19] |
| 4. | Modified sawdust | 32.3 | [20] |
| 5. | Hazelnut shell | 38.22 | [21] |
| 6. | Walnut sawdust | 59.17 | [22] |
| 7. | Peanut hull | 68.03 | [23] |
| 8. | Garlic peel | 82.64 | [24] |
| 9. | Tea wood bark | 84 | [19] |
| 10. | Dehydrated peanut hull | 108.6 | [25] |
| 11. | Cedar sawdust | 142.36 | [26] |
| 12. | Gulmohar (*Delonix regia*) plant leaf powder | 186.22 | [27] |

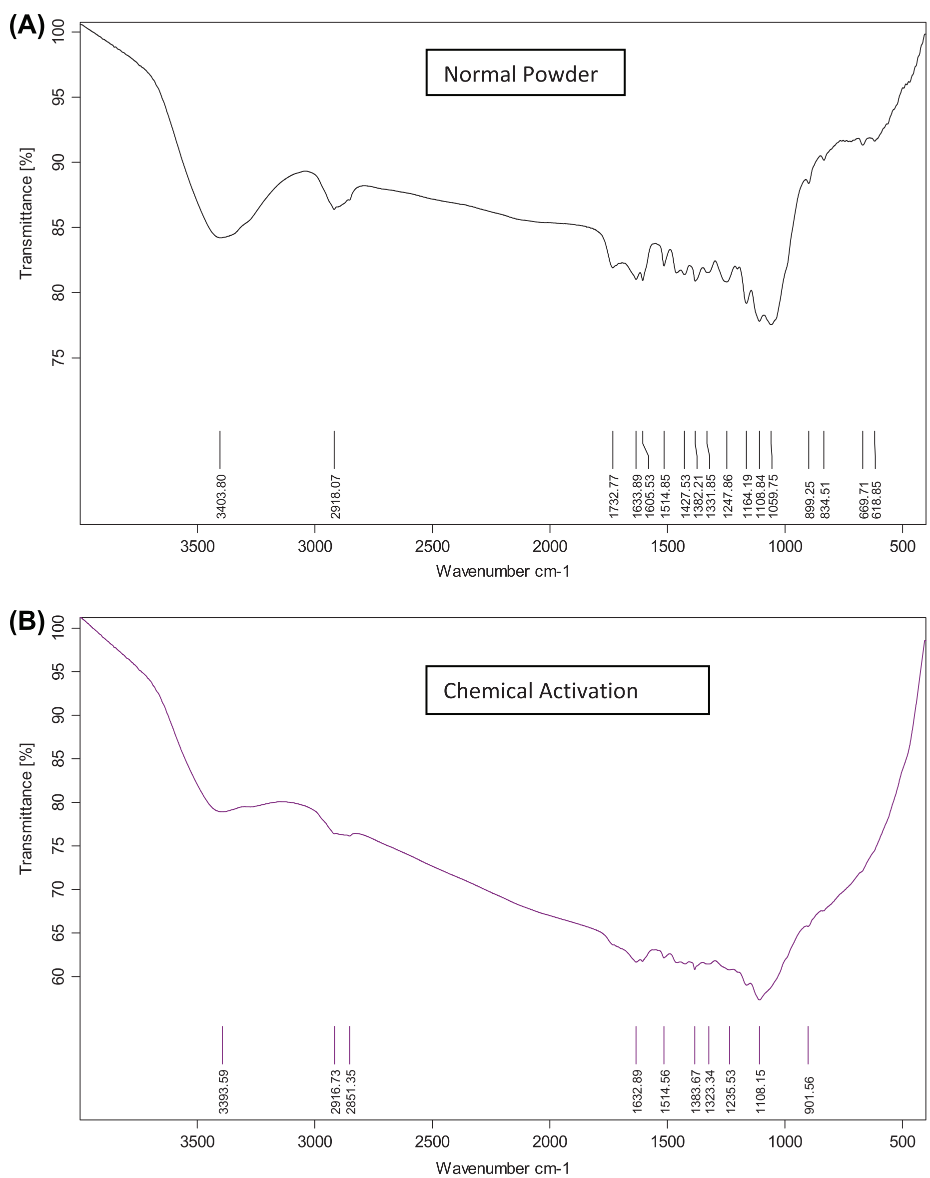


Fig. 5. SEM analysis of sugarcane bagasse: (A) normal powder and (B) chemically activated.

groups. The absorption at 3,400–3,440 $cm^{-1}$ represents the stretching of –OH groups, which was reduced after $K_2HPO_4$ treatment. It specified that partial hydrogen bonds of cellulose were destroyed, leading to an enhanced accessibility of cellulose to reagents. The peak at 2,920–2,930 $cm^{-1}$ represents the C–H stretching, the decrease in content indicated that methyl and methylene of cellulose had some rupture. The contents of the functional groups mentioned above were all decreased after $K_2HPO_4$ treatment. However, slight changes were found for some functional groups. Thus, results of IR spectrum indicates that, chemically activated powder shows some functional group changes and assists in higher adsorption capacities of chemically treated sample.

Scanning electron micrographs were depicted in Fig. 6(A) and (B) for normal and chemically activated bagasse powder. Normal powder micrograph shows slightly organized surface topological characteristic of bagasse particles prior to chemical activation. After the chemical activation in batch process, bagasse fibrous were swollen and distorted. Surface of bagasse fiber was modified by $K_2HPO_4$ activation.

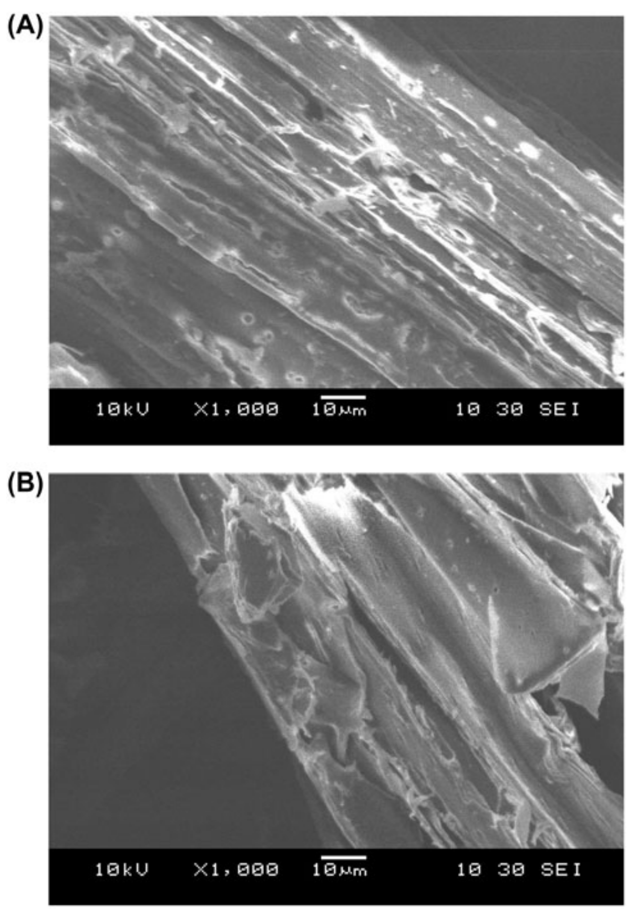


Fig. 6. SEM analysis of sugarcane bagasse: (A) normal powder and (B) chemically activated.

## 4. Conclusion

Sugarcane bagasse was explored as an adsorbent using chemical activation in the presence of $K_2HPO_4$ using batch studies. The preparation of adsorbent was optimized by one-factor-at-a time method, and optimum conditions were found to be $K_2HPO_4$ concentration (2 M), impregnation time (6 h), temperature (30˚C), and impregnation ratio (0.0125 g/mL). The maximum adsorption capacity was found to be 136.84 mg/g for the powdered adsorbent which was lower than the standard activated carbon (236 mg/g). Infrared spectroscopy and SEM results supported the chemical activation of bagasse powder for maximum adsorption capacity. However, the proposed protocol delivers cost-effective adsorbent for the removal of hazardous dyes from polluted water streams as compared to costly activated carbon.

## References

[1] H.S. Ashoka, S.S. Inamdar, Adsorption removal of methyl red from aqueous solutions with treated sugarcane bagasse and activated carbon—A comparative study, Global J. Environ. Res. 4(3) (2010) 175–182.

[2] M.A.R.A. Khan Rao, S. Anwar, J. Ahmad, R. Ahmad, Adsorption studies on rice husk: Removal and recovery of Cd(II) from wastewater, Bioresour. Technol. 86 (2) (2003) 147–149.

[3] J. Song, W. Zou, Y. Bian, F. Su, R. Han, Adsorption characteristics of methylene blue by peanut husk in batch and column modes, Desalination 265(1–3) (2011) 119–125.

[4] S. Noreen, H.N. Bhatti, S. Nausheen, S. Sadaf, M. Ashfaq, Batch and fixed bed adsorption study for the removal of Drimarine Black CL-B dye from aqueous solution using a lignocellulosic waste: A cost affective adsorbent, Ind. Crops Prod. 50 (2013) 568–579.

[5] S. Sadaf, H.N. Bhatti, Batch and fixed bed column studies for the removal of Indosol Yellow BG dye by peanut husk, J. Taiwan Inst. Chem. Eng. 45(2) (2014) 541–553.

[6] V. Vadivelan, K.V. Kumar, Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk, J. Colloid Interface Sci. 286(1) (2005) 90–100.

[7] V.K. Gupta, A. Mittal, R. Jain, M. Mathur, S. Sikarwar, Adsorption of Safranin-T from wastewater using waste materials—Activated carbon and activated rice husks, J. Colloid Interface Sci. 303(1) (2006) 80–86.

[8] I.A.W. Tan, A.L. Ahmad, B.H. Hameed, Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: Equilibrium, kinetic and thermodynamic studies, J. Hazard. Mater. 154(1–3) (2008) 337–346.

[9] F.D. Ardejani, Kh. Badii, N.Y. Limaee, S.Z. Shafaei, A.R. Mirhabibi, Adsorption of Direct Red 80 dye from aqueous solution onto almond shells: Effect of pH, initial concentration and shell type, J. Hazard. Mater. 151 (2–3) (2008) 730–737

[10] C. Namasivayam, D. Kavitha, Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste, Dyes Pigm. 54(1) (2002) 47–58.

[11] V.K. Garg, R. Gupta, A.B. Yadav, R. Kumar, Dye removal from aqueous solution by adsorption on treated sawdust, Bioresour. Technol. 89(2) (2003) 121–124.

[12] I.A.W. Tan, B.H. Hameed, A.L. Ahmad, Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon, Chem. Eng. J. 127 (2007) 111–119.

[13] E.C. Khoo, S.T. Ong, S.T. Ha, Removal of basic dyes from aqueous environment in single and binary systems by sugarcane bagasse in a fixed-bed column, Desalin. Water Treat. 37 (2012) 215–222.

[14] S.T. Ong, E.C. Khoo, P.S. Keng, S.L. Hii, S.L. Lee, Y.T. Hung, S.T. Ha, Plackett–Burman design and response surface methodological approach to optimize basic dyes removal using sugarcane bagasse, Desalin. Water Treat. 25 (2011) 310–318.

[15] S.T. Ong, E.C. Khoo, S.L. Hii, S.T. Ha, Utilization of sugarcane bagasse for removal of basic dyes from aqueous environment in single and binary systems, Desalin. Water Treat. 20 (2010) 86–95.

[16] S. Sadaf, H.N. Bhatti, S. Ali, K.U. Rehman, Removal of Indosol Turquoise FBL dye from aqueous solution by bagasse, a low cost agricultural waste: Batch and column study, Desalin. Water Treat. 52 (2014) 184–198.

[17] S. Zaheer, H.N. Bhatti, S. Sadaf, Y. Safa, M. Zia-ur-Rehman, Biosorption characteristics of sugarcane bagasse for the removal of foron blue e-bl dye from aqueous solutions, J. Anim. Plant Sci. 24(1) (2014) 272–278.

[18] G. Annadurai, R. Juang, D. Lee, Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, J. Hazard. Mater. 92 (2002) 263–274.

[19] G. McKay, G. Ramprasad, P. Pratapa Mowli, Equilibrium studies for the adsorption of dyestuffs from aqueous solutions by low-cost materials, Water Air Soil Pollut. 29 (1986) 273–283.

[20] D.S. De, J.K. Basu, Adsorption of methylene blue on to a low cost adsorbent developed from sawdust, Indian J. Environ. Prot. 19 (1998) 416–421.

[21] M. Doğan, H. Abak, M. Alkan, Biosorption of methylene blue from aqueous solutions by hazelnut shells: Equilibrium, parameters and isotherms, Water Air Soil Pollut. 192 (2008) 141–153.

[22] F. Ferrero, Dye removal by low cost adsorbents: Hazelnut shells in comparison with wood sawdust, J. Hazard. Mater. 142 (2007) 144–152.

[23] R. Gong, M. Li, C. Yang, Y. Sun, J. Chen, Removal of cationic dyes from aqueous solution by adsorption on peanut hull, J. Hazard. Mater. 121 (2005) 247–250.

[24] B.H. Hameed, A.A. Ahmad, Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass, J. Hazard. Mater. 164 (2009) 870–875.

[25] D. Özer, G. Dursun, A. Özer, Methylene blue adsorption from aqueous solution by dehydrated peanut hull, J. Hazard. Mater. 144 (2007) 171–179.

[26] O. Hamdaoui, Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick, J. Hazard. Mater. 135 (2006) 264–273.

[27] V. Ponnusami, V. Gunasekar, S.N. Srivastava, Kinetics of methylene blue removal from aqueous solution using gulmohar (*Delonix regia*) plant leaf powder: Multivariate regression analysis, J. Hazard. Mater. 169 (2009) 119–127.