Analysis of Adsorptive characteristics of chemically modified bio-waste walnut shell for degradation of Brilliant yellow dye

Vijeta arora[1] & Dinesh Pratap tiwari[2]
[1]Chemical Engineering Department,
Deenbandhu Chhotu Ram University of Science and Technology, Sonipat, Haryana, India.
[2]Director/Principal (on deputation), Rajiv Gandhi Government Engineering College, Kangra(HP) and Professor, Department of Chemical Engineering, Deenbandhu Chhotu Ram University of Science and Technology, Sonipat, Haryana, India.

Received: March 05, 2019 Accepted: April 15, 2019

ABSTRACT: *In the present study, activated walnut shell powder (AWSP) was fabricated by chemical modification of waste walnut shell using sulphuric acid activation method. The AWSP formed was analyzed under different sets of batch experiments to observe the adsorption characteristics on brilliant yellow (BY) dye. Influence of different parameters such as BY concentration, amount of dose, pH and contact time was observed and optimum conditions has been calculated. Various characterization techniques SEM, BET, FTIR were applied to understand morphology, surface area and presence of various functional groups on the adsorbent. The interaction between adsorbate and adsorbent was further investigated by applying Langmuir, Freundlich and Temkin Isotherms where Langmuir shows best suitability with regression coefficient > 0.9. Maximum removal efficiency accounted for 90% under optimized parameters. This work offers an ecofriendly and economic removal of Industrial dye BY using AWSP adsorbent.*

1. Introduction

Growth of Industries has left significant impact on ecosystem with the positive impression of serving mankind. Different Industries such as textile, paper, pharmaceuticals[1], food, leather, paint uses dyes for coloring their products and the effluents from these industries are discharged directly to water bodies without prior treatment in some cases and may be up to the permissible limit. Textile industries discharged around 15% of dyes produced annually[2]. Presence of dyes even at small amount is matter of concern for the health of human being, flora and fauna and aquatic life due to the harmful toxological and carcinogenic nature of dyes[3]. Dyes can cause allergic problems, dysfunction of kidney and reproductive systems, skin irritation in human being whereas environmental problems accounts for reduction in sunlight penetration, inhibiting photosynthesis, Increasing BOD and COD. Thus, the need to protect mankind, aquatic life and environment develops the interest of researchers to investigate the possible removal methods of dyes from waste water. From years, numerous methods such as aerobic and anerobic treatment, coagulation, flocculation, filtration, ozonation, Adsorption, reverse osmosis, advance oxidation methods[4]. Inspite the efficiency of all these methods, adsorption is considered to be the best method in terms of its applicability[5] and it also proved as effective physical method to eliminate or lower the pollutant or color concentration considering all its advantages and disadvantages. Literature shows wide range of available natural and synthetic adsorbents that have been used for degradation of dyes. The adsorbents include agro waste, activated charcoal, zeolites, nano materials. The lignin cellulosic materials such as nut shells and fruit stones are good precursors for production of activated carbons[6-10]

In the present work, the cellulose agricultural waste material walnut shell was converted into original powder form using pulverizer and grinder, after that it was chemically modified to activated form AWSP using H_2SO_4 activation method. Walnut shell was chosen as they are generally discarded as waste material and can be easily collected on a community basis. The functional groups determined by FTIR help in adsorbing dye by electrostatic interaction, dipole-dipole and hydrogen bonding. Chemical activation was done in order to achieve highly developed homogenous and porous particles.[11]

2. Materials and Methods.

2.1 Adsorbate

BY dye was purchased from jay chemicals industries Ltd. (Ahmedabad) India and was used without any further modification and purification .The stock solution of (100 mg/l) BY dye was prepared by dissolving required amount of dye in distilled water and further dilutions can be done according to the experimental requirement

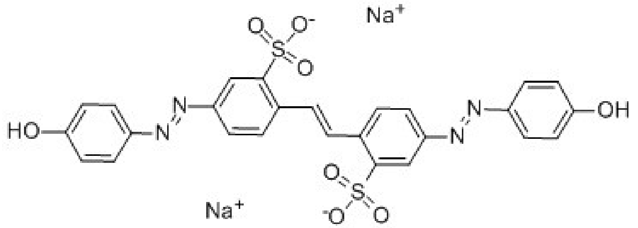

Figure 1. Structure of BY dye

2.2 Adsorbent

Walnut shell was collected from sweet shop of city centre market. The shells were initially washed using distilled water, kept for sun drying for a period of 2 hours, temperature recorded was 35°C, thereafter shell was pulverized and grounded to powder form. This brown powder was further subjected to modification by impregnating with concentrated sulphuric acid by 1:1 weight ratio. Solution was stirred and kept for 24hours. After it was thoroughly washed to neutralize the effect of acid till pH attain 7 value the sample was kept for drying in the muffle furnace at temperature of 500°C. Finally the powder was collected and stored in air tight container for carrying subsequent experiments.

Figure 2. conversion from walnut shell to activated carbon

2.3. Adsorption studies

Batch adsorption equilibrium experiments were carried out at room temperature 30°C for the adsorption of BY dye on AWSP adsorbent. The effects of parameters such as initial concentration, pH, dosage and contact time were investigated on adsorption uptake. Sample solutions were stirred with agitation speed 120rpm for 2 hours to attain equilibrium. The BR concentration after equilibrium adsorption was measured by using UV-VIS spectrophotometer (ultra-3660) at 551nm. The amount of dye adsorbed at equilibrium, q_e(mg/g) was calculated by:

$q_e(C_0 – C_e)V/W$.

Where C_0 and C_e (mg/l) are liquid phase concentrations of BY at initial and at equilibrium.

3. Results and Discussions

3.1 Effect of initial BY concentration

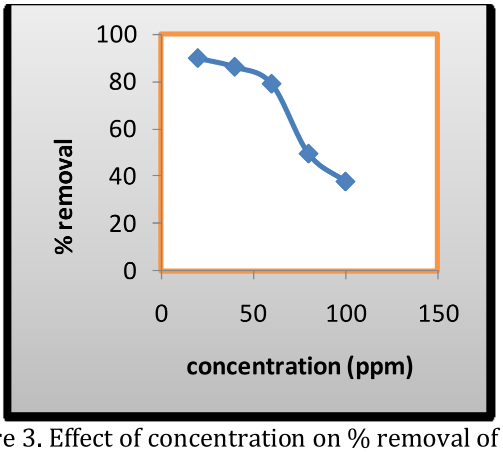

Figure 3. Effect of concentration on % removal of BY dye.

Five different samples of varying concentration (20,40,60,80,100mg/l) with 0.1g of adsorbent were analysed, it was observed from fig. 3. As the initial dye concentration increases from 20 to100mg/l, the removal percentage decreases from 90% to 38% because at initial stage, dye sorption was fast and gradually it became slower because more number of surface sites are available initially for adsorption and with lapse of time the repulsive force between solute molecules and bulk phases[4] increases which leads to difficulty in remaining sites to be occupied and thus decrease in removal efficiency. Maximum removal efficiency was reported to be 90%.

3.2 Effect of contact time

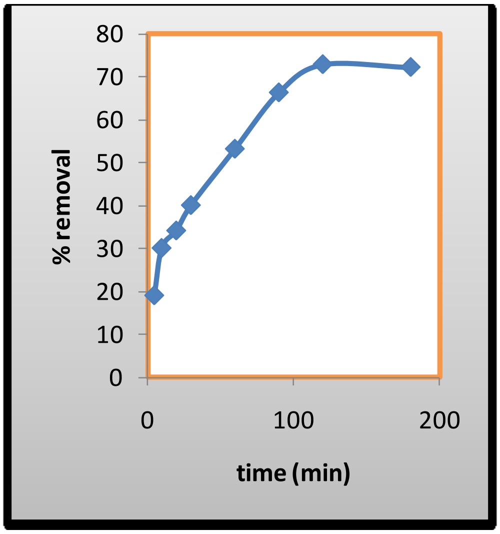

Figure 4. Effect of contact time on % removal of BY dye.

The effect was analysed by taking five different samples of fixed concentration (30mg/l) with 0.1 g of adsorbent dose and time variation is kept from (5 to 120min).The fig.4 shows longer contact time was required by BY dye to reach equilibrium and maximum removal efficiency achieved was 72%.

3.3 Effect of adsorbent dosage

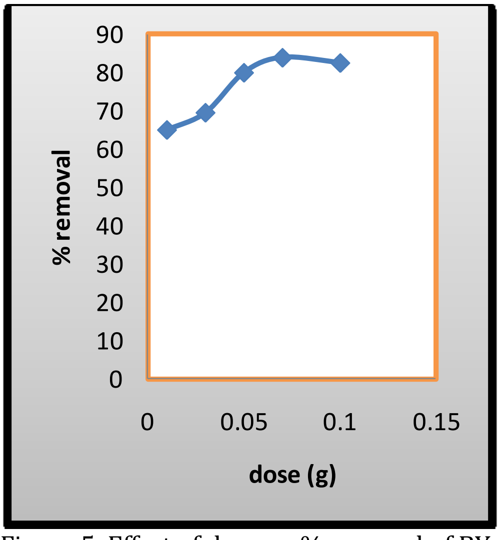

Figure 5. Effect of dose on % removal of BY dye

Five different samples of fixed concentration (30mg/l) with varying adsorbent dose (0.01, 0.03, 0.05, 0.07, 0.1 g) and fixed time 120min. were analysed. It was observed from fig.5. the percentage adsorption increases with increase in dosage due to the availability of more adsorption sites[5] and increased surface area. Maximum removal was found to be 83%.

3.4 Effect of pH

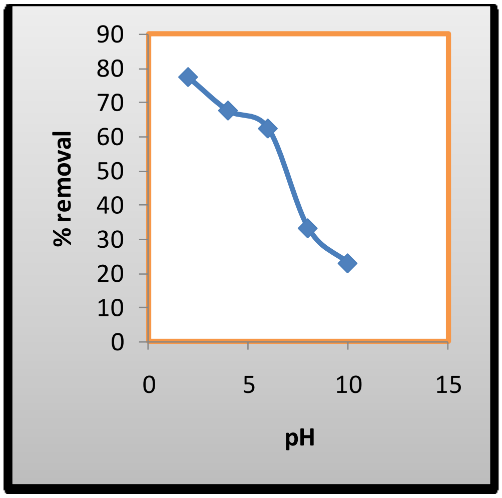

Figure 6. Effect of pH on % removal of BY dye

The effect of pH was shown in fig. 6, BY removal was found to significantly decrease with increase in pH and the maximum removal achieved is 78%. It was explained at lower pH, the positive charge on surface sites increases which favour adsorption of anionic dye due to electrostatic force of attraction.

3.5 Adsorption Isotherms

The adsorption study of BY dye on AWSP adsorbent was determined by Langmuir, Freundlich and Temkin Isotherm.

Langmuir Isotherm

Langmuir Isotherm model represented by fig.7 describe homogenous nature of adsorbent surface with the presence of active sites having uniform energy (J). Once monolayer is achieved, adsorption is no longer influenced by solute transport.(k).Langmuir Isotherm equation is given by [12]:

$C_e/q_e = 1/b.qm + C_e/q_m$(1)

Where C_e is the dye concentration in solution at equilibrium (mgL^{-1})

q_e is the amount of adsorbed dye at equilibrium (mgg^{-1})

q_m is the maximum amount of adsorbed dye (mgg^{-1})

b is the equilibrium constant (L mg^{-1}),

q_m is calculated from slope and intercept of the straight line obtained by plotting C_e/q_e vs C_e

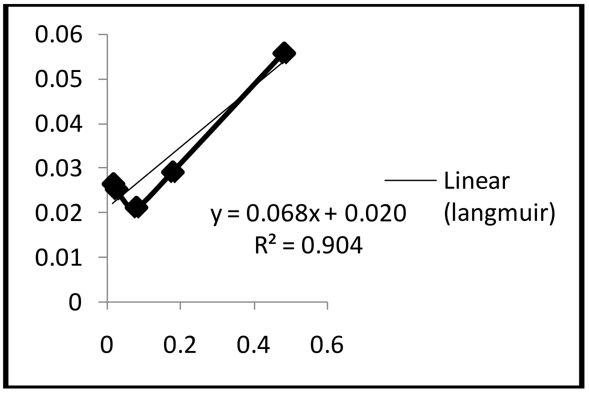

Figure 7. Langmuir plot

Freundlich Isotherm

Isotherm represented by fig.8 describes the heterogeneous system and reversible adsorption. Freundlich Isotherm equation is given by (2):

Log q_e= logK_F + 1/n log C_e (2)

Where, C_e is the dye concentration in solution at equilibrium (mgL^{-1})

q_e is the amount of adsorbed dye at equilibrium (mgg^{-1})

K_F ($(mg/g)(L/mg)^{1/n}$)

n is constant affecting the adsorption process by adsorption capacity and adsorption intensity.

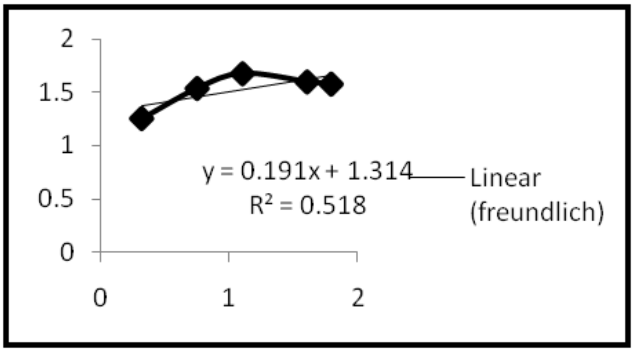

Figure 8. Freundlich plot

Temkin Isotherm

The Temkin Isotherm represented by fig.9 constants (A and B) were obtained from the plot of $q_e$vs lnC_e.
Temkin Isotherm equation is given by (3):

q_e= B ln A + B lnC_e (3)

Where, A is equilibrium constant (Lg^{-1}) representing maximum binding energy
B (j mol^{-1}) is the heat of adsorption
B= RT/b_T, $b_T$is Temkin isotherm energy constant (j mol^{-1}), R is universal gas constant

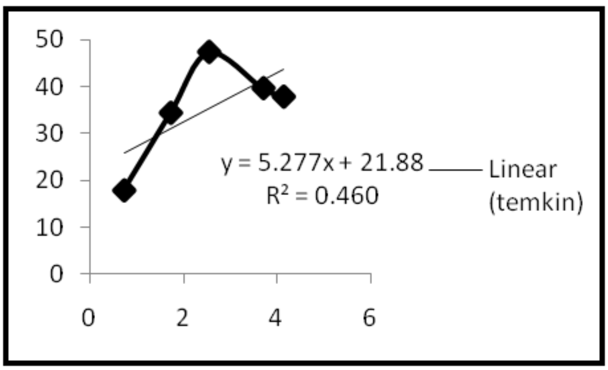

Figure 9. Temkin plot

4. Characterization of AWSP

4.1 BET

B.E.T surface area of AWP was found to be 122.67 m^2/g , total pore Volume 0.087 cc/g and pore diameter D_v(d) 3.346nm. High surface area of AWSP was due to the activation process as after the activation process, volatile matter content decreases and fixed carbon content increases.

4.2 SEM

The surface morphology has been studied by SEM (Scanning electron microscopy)[6]. Shows that the surface was uneven, rough and the presence of large pores enhances adsorption capacity as shown in fig.10.

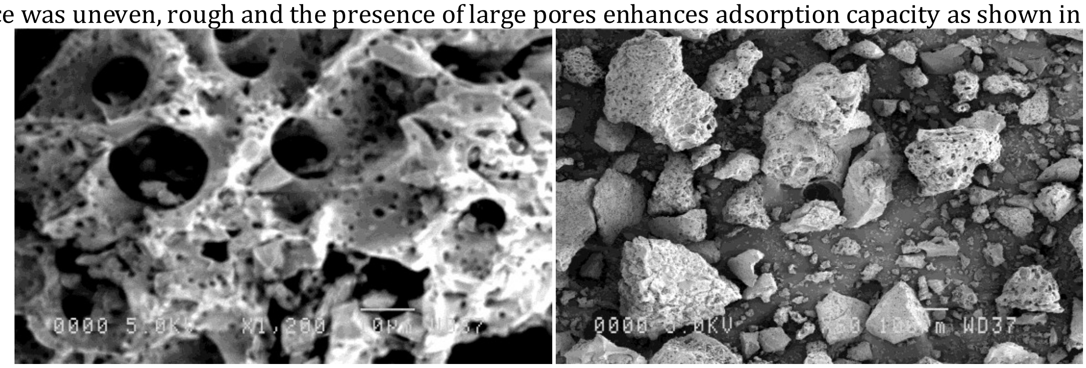

Figure 10. SEM images of AWSP adsorbent.

4.3 FTIR

FTIR spectra of AWSP adsorbent was measured in the spectral range of 4000 to 500 cm^{-1} with a resolution of 4cm by using FTIR spectra (Shimadzu – 8400, japan). The FTIR technique determines chemical bonds of unknown sample. FTIR spectra describes the adsorbent-adsorbate interaction. The peaks represents various functional groups on the surface of AWSP adsorbent which shows that the adsorbent surface is enriched with functional groups for carrying the adsorption of dye. Important peak was observed at 3421.5 cm^{-1} which shows presence of hydroxyl group, broadband region 1700 cm^{-1} to 1800 cm^{-1} corresponds to C=O stretching non-ionic carboxyl groups.

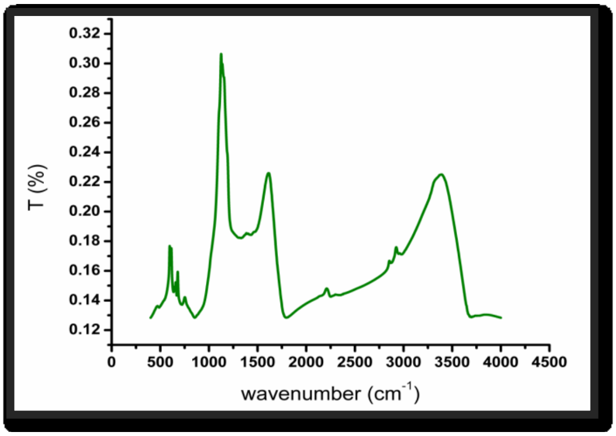

Figure 11. FTIR spectra

Conclusion

The investigation shows the applicability of AWSP as a low cost and efficient adsorbent with high adsorption capacity. In the experimental batch study, the optimized parameters have been analyzed for maximum adsorption. The result shows effective pH to be 2, the adsorbent dosage is 0.1g for each 20ml sample and mixing time is 2h. At these conditions, maximum removal efficiency achieved was 90%. The isotherms were well fitted but Langmuir model favors the adsorption process which denotes monolayer adsorption with high regression coefficient >0.90. Further characterization studies indicate the feasibility of using AWSP as promising adsorbent. The degradation study of BY dye using prepared AWSP proved to be a successful and efficient approach for the dye removal in an economic manner and also helpful in maintaining the solid waste management.

References

1. T.N. Ramesh, D.V. Kirana, A. Ashwini and T.R. Manasa, J. Saudi. Chem. Soc., 21, 165 (2017).
2. S.E. Subramani and N.Thinakaran. J. Proc. Safety and Envt. Prot., 106. 1(2017)
3. A.M. Aljeboree, A.N. Alshirifi and A.F. Alkaim. Arabian J. Chem. 10. 381(2017)
4. M.A. Ahmad and R. Alrozi. Chem. Engg. J., 171. 510 (2011).
5. A. Salama. J. Coll. Int. Sci., 487. 348 (2017).
6. W. Heschel and E. Klose. Fuel., 74. 1786 (1995)
7. K. Gergova and S. Eser. Carbon., 34. 879 (1996)
8. A. Marcilla. S.G. Garcia. M. Asensio and J.A. Conoesa. Carbon., 38. 429 (2000).
9. Z. Hu and E.F. Vansant. Micropor. Mater., 3. 603 (1995).
10. S. Balci. T. Dogu and H. Yucel. J. Chem. Tech. Biotechnol., 60. 419 (1994).
11. M. M. Sabio and F.R. Reinoso. Colloids and Surf. A., 241. 15 (2004).
12. N. Belhouchat, H. Zaghouane-Boudiaf, and C. Viseras, "Removal of anionic and cationic dyes from aqueous solution with activated organo-bentonite/sodium alginate encapsulated beads," Appl. Clay Sci., vol. 135, pp. 9–15, 2017.