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Treatment of dyes contaminated water using surfactants modified activated carbon derived from rice husk

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ABSTRACT

In the present work, the surfactant modified activated carbon (AC) was used for the elimination of water soluble dyes, i.e. methylene blue (MB) and crystal violet (CV) dyes from aqueous solutions. The AC was prepared from rice husk by carbonization process, and then activated by treatment with zinc chloride ($ZnCl_2$). The AC was further modified by sodium dodecyl sulfate (SDS) and sodium cupryl acetate (SCA) surfactants. The AC, SDS/AC and spent SDS/AC were characterized by SEM, FT-IR, XRD and EDX analysis. Under optimized conditions the adsorption was found to be better as compared to be AC and SCA/AC, under which maximum adsorption of MB and CV over SDS/AC was found to be 90% and 85%, respectively. Kinetic and isotherm studies revealed that adsorption of both dyes over SDS/AC occur through pseudo-second-order kinetics and follow the Freundlich adsorption isotherm model. The various thermodynamic parameters, like $\Delta G°$, $\Delta H°$ and $\Delta S°$ shown that the process of adsorption dyes over SDS/AC was an endothermic and spontaneous process. According to the data analysis that % removal of MB using AC, SCA/AC and SDS/AC was 75%, 83% and 84.86%, separately, while using same adsorbents the % removal of CV was 31.5%, 79% and 84.94%, respectively. It is clear from these consequences that the adsorption effectiveness of the AC was significantly enhanced with the surfactant modification. Findings from this study suggest that SDS/AC could be utilized as a promising adsorbent at the same time eliminating MB and CV from wastewater.

Keywords: Activated carbon; Modified activated carbon; Adsorption; Surfactants; Dyes

1. Introduction

It is well known that water is a fundamental natural resource for the existence of life on the earth's surface [1]. Due to the industrial revolution and anthropogenic activities the purity of safe drinking water and its availability at risk in present and more severe in future. Amongst the concerns of that reckless development, the environmental pollution has become a serious aspect [2]. Various types of chemical compounds accumulate in water from many sources like household [3], vehicles [4], agriculture [5], and industries [6] and convert it into wastewater, which is unsuitable for reuse. Wastewater, having deadly poisonous

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compounds is a major threat for humans and for the whole ecosphere as well. Harmful substances have been found because of the industrial wastes, urban and agricultural pollutants, and the use of insecticides, pesticides and fertilizers [7]. Lethal pollution may cause an acute or a chronic influence on the environment. The major water pollutants include heavy metals, inorganic and organic compounds, synthetic polymers, hydrocarbons, pharmaceuticals, personal care products and dyes [8]. Heavy metals such as V, Cr, Fe, Mn, Cd, Pb, Zn, etc. have been observed to be lethal to various forms of life. They are stored in living tissues and concentrate throughout the whole food web [9]. Similarly, organic compounds like dyes which have important applications in textile industries also a major pollutant of water and turn it to miss fit for any further use [10].

Many techniques have been introduced to remove the pollutants in general and dyes molecule in particular from wastewater like catalysis [11], photo degradation [12], adsorption [13], ion exchange [14], and oxidation [15]. Among these methods, the adsorption method has attracted the researcher's interest for removing the highly toxic pollutants from wastewater due to its high efficiency, simplicity, flexibility, economic impact and it is easy to deal with. In this process, electrostatic interaction between the adsorbate and adsorbent surfaces is occurred. Several adsorbents have been used for removing of dyes from water, for example, AC and nanomaterials. These materials have high surface area and porosity as well as chemical and thermal stability [16].

Most of materials which have high carbon content and low inorganic component could be used as raw materials for AC production. The most abundant renewable resources are the agricultural by-products which produce in huge quantities. These wastes cause many problems during their disposal therefore there is a need to increase the value of these inexpensive by-products. Thus, converting these wastes into AC will add a significant economic value and decrease the waste disposal [17]. Many different adsorbent's were synthesized for adsorption purpose like biochar/bentonite/waste polystyrene and biochar/bentonite/waste polyethylene terephthalate [18,19], zeolite and clay [20,21], chitosan based composites [22], certain agricultural wastes [23], wood based saw dust [24], nanomaterial's and their composites [8], biomass solid waste based activated carbon [25], activated carbon [26,27], rice husk based activated carbon [28], activated carbon obtained by $ZnCl_2$ activation of acorn shell [29], zinc oxide nanoparticles loaded on activated carbon [30], silica nanoparticles grafted with copolymer of acrylic acrylamide [31], bio-based magnetic activated carbon [32], magnetic AC/CeO_2 nanocomposite [33], bone bio-char [34], activated carbon from Phoenix dactylifera fruit pits [35], dodecyl sulfate chain anchored mesoporous grapheme [36], hydrochar [37], carbon based polymeric nanocomposites [38], silica coated copper ferrite decorated oxidized multi-walled carbon nanotubes nanocomposite [39], solvent impregnated resin [40], nanomagnetic copper ferrite/drumstick pod biomass composite [41], and cetyltrimethyl ammonium bromide intercalated and branched polyhydroxystyrene functionalized montmorillonite nano-composite [42]. The activated carbon based adsorbent selection is due to its greater surface area, structural porosity of high grade, better thermal stability, neutral, cationic and anionic functional groups which in turn provide a high stability in acidic and basic medium [43]. Furthermore the rice husk (RH) activated carbon was modified by many ways and chemicals to increase the porosities, surface area or functionalities [44].

The main goal of this study is the utilization of RH waste in synthesis of modified activated carbon using surfactants and $ZnCl_2$ to increase the functionalities and porosity of the synthesized materials for removing of the MB and CV from aqueous solution. The process for preparation of AC is relatively low-cost and effective method since alternative source as RH is utilized. The studying of all parameters for preparation and adsorptions processes is the main objective of the present work.

2. Experimental

2.1. Materials and chemicals reagents

In the current work, all utilized chemicals and reagents were highly pure. $ZnCl_2$ (Merck), NaOH (CHEM-Lab), HCl (CHEM-Lab), Crystal Violet (CV) (Sigma-Aldrich), methylene blue (MB) (Sigma-Aldrich), sodium dodecyl sulfate (SDS) (Sigma-Aldrich) and sodium cupryl acetate (SCA) (Sigma-Aldrich) were used. RH was used as a raw material for production of AC. The desired concentrations of diluted MB and CV solutions were prepared and stored in a dark place to prevent the direct sunlight which may cause decomposition.

2.2. Preparation and characterization of activated carbon

The AC was prepared from RH by carbonization process. The RH was washed with double distilled water and then dried. Stoichiometric amount of RH was charged into a crucible, and carbonized in a furnace at 250°C for 5 h. The carbonaceous residue was ground to powder (ranging from 75 to 100 Micron) and then sieve through 100 mesh sieve. The carbonized char obtained from RH was activated by chemical treatment. The calculated amount (approximately 5 g) of carbonaceous mass obtained by carbonization of RH was mixed with 100 mL of $ZnCl_2$ (60% W/V) solution and stirred for 8 h at ambient temperature. The mixture was filtered to collect the carbon residue, washed with distilled water, and then dried at the 105°C for 3 h under nitrogen atmosphere. Surfactant-modified activated carbon was prepared by impregnation of sodium dodecyl sulphate (SDS) and sodium cupryl acetate (SCA) on the AC. The known weight of AC was added to 100 mL of surfactant solution (2%) and stirred at room temperature for 5 h. The mixture was then filtered and washed with distilled water several times to remove undesirable impurities. The final product was then dried at 40°C overnight. The SDS and SCA modified activated carbon was coded as SDS/AC and SCA/AC.

The AC, SDS/AC and SCA/AC were characterized by various instrumental analyses. FT-IR analysis of AC and SDS/AC carried out by FT-IR spectrophotometer (Parkin Elmer). The spectra were collected as an average of 3 scans between the wavelength range of 500–4,000 cm^{-1}. The textual

and morphological features of the AC and surfactant modified AC was investigated by scanning electron microscopy, using the SEM Model JEOL, Japan. The elemental analysis of the samples was determined by EDX detector. The crystallinity of the AC and the surfactant modified AC sample was investigated by X-ray diffractometer (Xpert Philip), using CuKα as the radiation source. While the concentration of the dyes in a solution was monitored by UV-Vis spectrophotometer (Shimadzu, Japan).

2.3. Adsorption process studies

All the experiments were performed in batch mode for each parameters like contact time, pH study, dose, concentration study, kinetic and thermodynamic studies. The concentration of dye in the solution was analyzed by UV-Vis spectrophotometer (Schimadzu, Japan). The absorbance of MB was measured at λ_{max} of 664 nm and that of crystal violet at λ_{max} 588 nm. Standard dye solutions of different concentrations were used to construct a calibration plot; the concentration of dyes was calculated from the absorbance with the help of calibration curve. The % removal of dyes after adsorption experiments was calculated by using following equation.

$$\%\text{Removal} = \frac{C_o - C_f}{C_o} \times 100 \tag{1}$$

where the C_o shows initial concentration and C_f represents the concentration of dye after time t.

2.4. Kinetic studies

The adsorption kinetics for the removal of MB and CV over SDS/AC was investigated by applying the adsorption data to the pseudo-first-order, pseudo-second-order and intra particle diffusion kinetic models. To investigate the pseudo-first-order kinetics, the following equation was used.

$$\ln\left(q_e - q_t\right) = \ln q_e - \ln K_1 t \tag{2}$$

where q_e (mg/g) is adsorption capacity of MB and CV dyes at the time of equilibrium, q_t (mg/g) is the amount of the dyes adsorbed at time t, K (min^{-1}) is pseudo-first-order rate constant and t is the time.

The pseudo-second-order kinetics was studied by using the following equation:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_t} \tag{3}$$

where t is the time, q_e (mg/g) is the maximum amount of MB and CV dye absorbed over SDS/AC at equilibrium, q_t (mg/g) is the amount of the dyes adsorbed at time t and K_2 (mg/g min) is the pseudo second order kinetics rate constant, which was calculated from the intercept of the plot of Eq. (3).

The adsorption data was also analyzed by intra particle diffusion kinetic model, which is represented by following equation as;

$$q_t = K_i t^{1/2} + C \tag{4}$$

where C is the constant related to the thickness of the boundary layer (mg/g), K_i is the intraparticle diffusion rate constant (mg/g $min^{1/2}$).

2.5. Adsorption isotherm

In order to investigate nature of the adsorption process, the adsorption data was interpreted by Langmuir and Freundlich isotherms models. The Freundlich isotherm is an empirical model which is represented by the following equation.

$$\ln q_e = \ln K_f - \frac{1}{n} \ln C_e \tag{5}$$

where q_e (mg/g) maximum amount of adsorbate adsorbed on adsorbent surface at the equilibrium, C_e (mg/L) show the equilibrium concentration (mg/L), and K_f and n are factors that depends on the adsorbate and adsorbent amounts.

This model represents the monolayer adsorption process on the surface of the adsorbent in a uniform manner to occupy the active sites of the adsorbent. The adsorption data was plotted by using the following equation as:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \tag{6}$$

where C_e (mg/L) is the equilibrium concentration of dye in the solution, q_e (mg/g) is the maximum amount of adsorbate adsorbed by adsorbent, q_{max} is the maximum adsorption capacity and b is Langmuir constant related to energy of adsorption.

3. Results and discussion

The adsorption of MB and CV dyes from aqueous solution was studied by using AC, SDS/AC and SCA/AC as an adsorbents. Initial batch mode adsorption experiments were carried at 25°C and for 60 min and initial dyes concentration of dye was 50 mg/L. The data show that % removal of MB using AC, SCA/AC and SDS/AC was 75%, 83% and 84.86%, respectively, whereas using same adsorbents the % removal of CV was 31.5%, 79% and 84.94%, respectively. It is clear from these results that the adsorption efficiency of the AC was significantly enhanced with the surfactant modification. Additionally, the SDS/AC led to high removal of both the dyes, that is, MB and CV as compared to SCA/AC. A number of studies show that SDS supported on activated carbon led to high removal of dyes [1]. As clear from the above discussion that the adsorption efficiency of SDS/AC was higher than SCA/AC, therefore SDS/AC was selected for further study based on the optimization concept.

3.1. Properties of AC and SDS/AC

The AC, surfactant modified activated carbon, that is, SDS/AC and spent SDS/AC was characterized by FT-IR,

SEM, XRD and EDX analysis. Detailed discussion on the results is given as follows.

3.1.1. FT-IR spectroscopy

The FT-IR spectra of AC and modified AC before and after adsorption of MB and CV are shown in Figs. 1 and 2. The FT-IR spectra of the AC shows, broad peak at around 3,500 cm^{-1}, which presented the O–H stretching vibrations for hydroxyl groups of surface water or carboxyl groups. Two peaks positioned at around 1,709 and 1,590 cm^{-1} shows the C=O of carbonyl or carboxyl and C=C of aromatic functionalities, respectively. A strong peak centered at 1,045 cm^{-1} corresponds to C–O stretching vibrations [45,46]. A medium peak appearing at 755 cm^{-1} indicates C–H out of plane deformation vibration [47]. These results indicate the characteristic functional groups of aromatic, carboxylic and oxygenate configurations of the typical activated carbon, which confirm the successful formation of activated carbon.

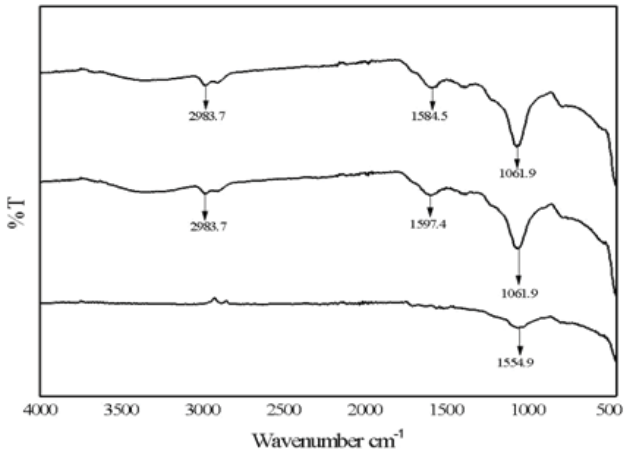

Fig. 1. FTIR spectra of AC before and after removal of CV and MB dyes.

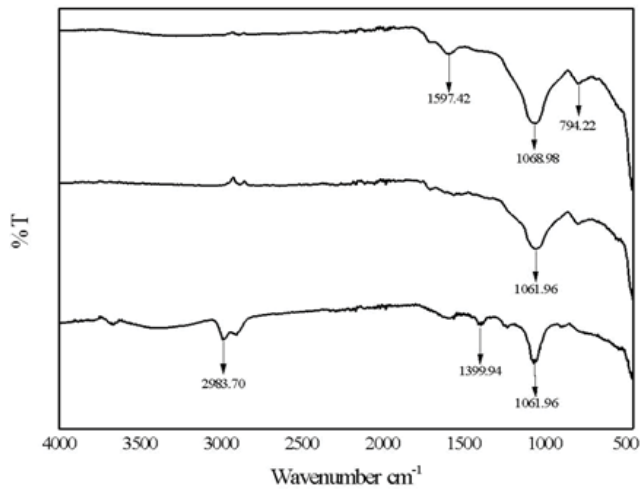

Fig. 2. FTIR spectra of SDS/AC before and after removal of CV and MB dyes.

The FT-IR spectra of AC (MB) and AC (CV) shows typical functional groups of the AC, with some changes in the peak intensities and in addition to some new peaks appeared. In case of both the samples, two new peaks appeared at 2,983 and 2,898 cm^{-1} which corresponds to C–H stretching vibrations of CH_3 and CH_2 groups, also in both samples the intensity of the peaks assigned to C=O and C–H (bending vibrations) is significantly decreased, which indicates the interaction of MB and CV onto the surface of AC.

The FT-IR spectra of SDS/AC and SDS/AC after adsorption of MB and CV, that is, SDS/AC (MB) and SDS/AC (CV) are shown in Fig. 2. The spectra of the SDS/AC show prominent peaks at 2,983 cm^{-1} which is the asymmetric stretching vibration of CH_3 group in –O–CH_3. This peak was found to be disappearing in case of MB and CV, respectively which show the physical interaction of dyes with the SDS/AC. Similarly, peak at 1,399 and 1061 cm^{-1} were found in pure SDS/AC, which are C–H asymmetric deformation vibration and –C–O– stretching vibration. However, both the peaks are disappearing in case of CV interaction with the SDS/AC while the peak 1,061 cm^{-1} shifted to 1,068 cm^{-1} in case of MB, which indicated a clear interaction of the synthesized SDS/AC with the organic dye materials. Furthermore, two peaks were observed in the case of 1,597 and 794 cm^{-1} in case of SDS/AC interaction with MB. These two peaks are actually the presence of C=C stretching vibration and C–H deformation vibration.

3.1.2. SEM analysis

The surface morphology of the AC and SDS/AC before and after adsorption of the MB and CV was investigated by SEM analysis. The SEM micrographs of AC, AC (CV) and AC (MB) is shown in Fig. 3. The SEM micrograph of AC shows that the surface of the AC is highly porous and rough, which is an important parameter for adsorption phenomena. The AC exhibit honeycomb like structure, with large number of pores which were extended to the internal cross section. These pores provide a large number of adsorption sites on the surface as well as inside the AC. The porosity and cavities facilitate the easy penetration of the solution inside the adsorbent and make the adsorption process effective and efficient. These results suggest that the AC exhibit excellent morphology, which is desirable for high adsorption capacity. The SEM micrographs of AC (MB) and AC (CV) shows high porosity but most of the pores are blinded, indicating the accumulation of the pollutants in the pores.

The SEM micrograph of SDS/AC exhibits folded and porous morphology, the surface seems layered and smooth, which may be due to impregnation of the surfactant. The micrographs of SDS/AC after adsorption of MB and CV shows similar morphology as that of original SDS/AC, which indicates that most of the dye molecules are adsorbed on the surface rather than the internal pore.

3.1.3. XRD Pattern analysis of AC and SDS modified AC

The XRD patterns of the rice husk derived AC and SDS/AC are shown in Fig. 4. The XRD pattern of AC shows a

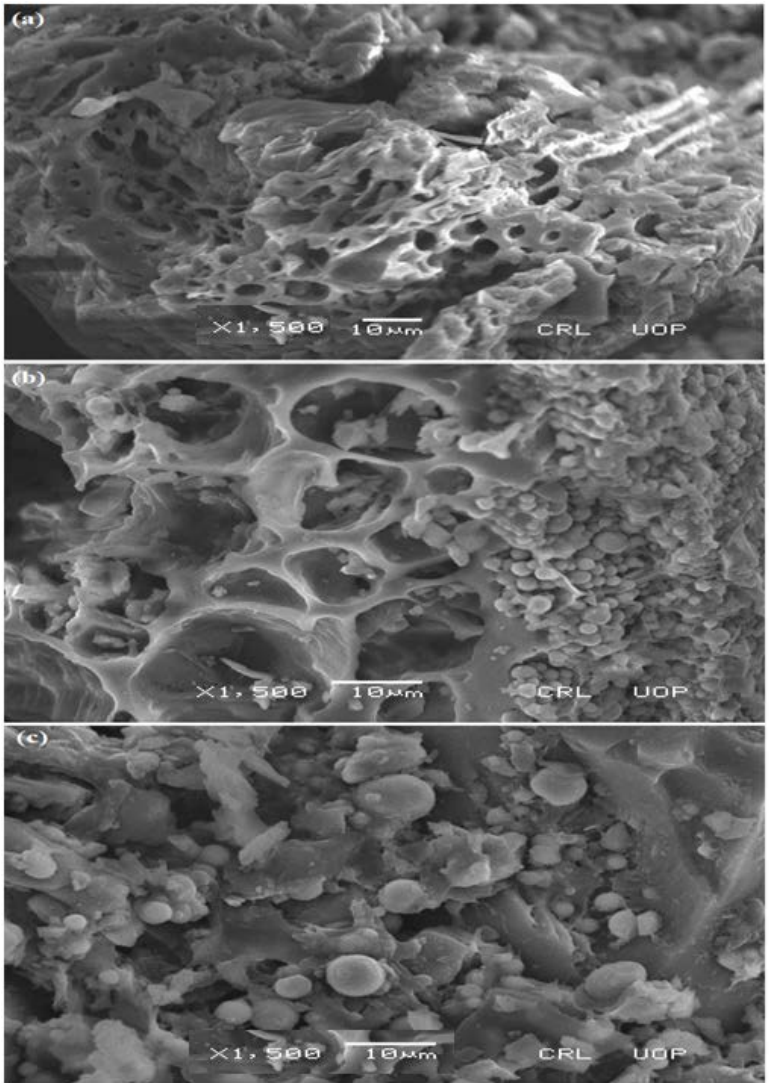

Fig. 3. SEM images of (a) SDS/AC, (b) SDS/AC after adsorption dye (MB) and (c) SDS/AC after adsorption dye (CV).

broad peak in the 2θ range of 20° to 23° which exhibit the characteristics amorphous carbon materials [32]. The XRD pattern of the SDS/AC also shows similar broad peak as that of AC, indicating the typical carbon material. The absence of additional broad peak suggests the complete removal of $ZnCl_2$ has occurred, which was used for chemical activation of carbonaceous material obtained from rice husk.

3.1.4. EDX analysis

The elemental composition of the AC, SDA/AC and SCA/AC weight % composition was investigated by EDX analysis (Fig. 5). The EDX signatures of elemental composition are shown in Table 1. In case of AC, the major element with high % weight, that is, 68.48% is carbon, it also comprises of other elements like hydrogen, nitrogen, oxygen, and sulfur. Typically the AC consist of about 88% C, 0.5% H, 0.5% N, 1.0% S, and 6% to 7% O [48]. These results show that the activated carbon is of good quality with high carbon content. The EDX profile of the SDA/AC and SCA/AC composite shows that the sample contains C, O, Zn, Ca and P in major proportion. The other elements present in the mineral matter of carbon are also present.

3.2. Optimization of adsorption parameters

After studying the efficiency of AC, SDS/AC and SCA/AC it was found that SDS modified activated carbon show better removal efficiency. Thus, for further optimization study SDS/AC was selected. In order to investigate the optimum conditions required for maximum removal of MB and CV dyes, adsorption was investigated under different conditions of concentration of dye, pH, time, temperature and adsorbent dose.

3.2.1. Effect of initial dye concentration

Adsorption of MB and CV over SDS/AC was studied under different initial concentration of dyes. The data are shown in Fig. 6, which shows that the % removal decreases

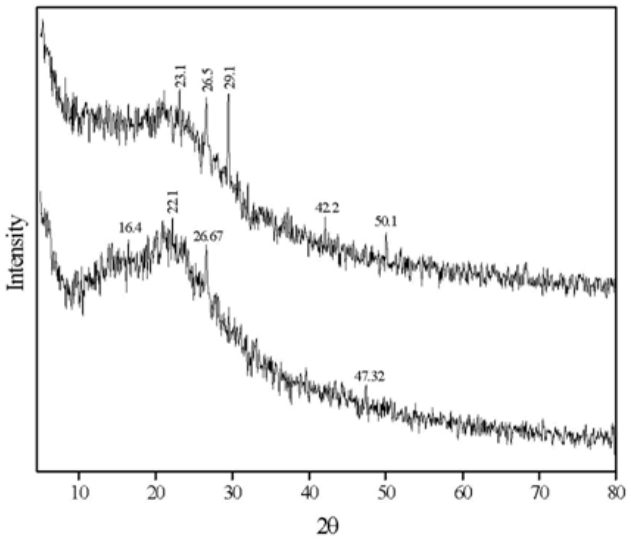

Fig. 4. XRD patterns of AC and SDS/AC.

Table 1
Elemental composition of AC, SDS/AC and SCA/AC

Elements	Weight %		
	AC	SDS/AC	SCA/AC
C	68.48	55.87	60.54
O	14.10	25.00	24.19
Cl	–	0.09	–
Na	–	0.17	–
Mg	0.47	0.22	0.29
Al	0.14	0.17	0.37
Si	10.89	7.41	9.08
S	0.30	0.34	0.12
K	2.88	0.52	0.52
Ca	0.70	0.27	0.86
Fe	0.57	0.21	0.50
P	1.47	0.56	0.94
N	–	6.36	–
Zn	–	2.81	2.60
Cu	–	0.53	–
Total	100	100	100

with increasing the initial concentration of both CV and MB from 5 to 50 mg/L. These results show that under high dyes concentration the active sites on the surface of the SDS/AC are occupied completely and no more sites are available on the given weight of the adsorbent surface which leads to decrease in the adsorption efficiency. It may be observed from the data that under 50 mg/L concentration, the amount of MB dye adsorbed on the SDS/AC was higher (88%) than the CV (84%). This may be attributed to the anionic nature of the surface of SDS/AC which shows high affinity for the cationic MB, as compared to CV. Therefore, the % removals in both cases were lower than 90% for higher concentration because the active sites may be occupied by the dyes molecules.

3.2.2. Effect of PH

The % removal of both CV and MB were studied at different pH, that is, 3, 5, 7 and 11 and results are indicated in Fig. 7. It can be observed from the data that the % removal of the both CV and MB increase with an increase in the pH value of the solution and reached up to 90% at pH 11. This is probably due to increase in the ionization of the surface of the materials while increasing the pH value of the solution. It is also clear from the results that the % removal value of the MB remains greater as compared to that of CV at different pH values, which may be due to the greater affinity of MB toward the modified-adsorbent material that in turn shows the selectivity of the materials. It can be suggested from the above discussion that the optimum pH for maximum removal of both the dyes over SDS/AC was found to be pH 11.

3.2.3. Adsorption capacity of SDS/AC

The adsorption capacity of per unit mass of the SDS/AC for MB and CV is shown in Fig. 8. The data shows that the adsorption capacity of the SDS/AC linearly increases with increasing the concentrations of both the dyes over SDS/AC. The results show that with the increase in the dyes concentration, the adsorption capacity also increases, and maximum adsorption capacity of MB and CV dyes were 9.53 and 9.04 mg/g of SDS/AC in the case of 50 mg/L solution of the dyes. The increase in the adsorption capacity was probably due to the availability of a large number of attractive electrostatic sites on the surface of the adsorbents for removal of dyes molecules from the solution [49].

3.2.4. Effect of contact time

The influence of adsorption duration on the removal of CV and MB over SDS/AC was studied at different time durations ranging from 15 min to 7 h. Results are indicated in Figs. 9 and 10 in which a plot of time (h) vs. q_t is given. The general trend in the data was that the adsorption capacity for different concentrations (mg/L) solutions increased with increasing the adsorption time. Initially, the adsorption of dyes was very fast which may be attributed to the availability of large surface area and greater number of electrostatic units on the surface of the SDS/AC. With the increase in the adsorption time, the adsorption capacity also increased, and became constant at 4 h in case of both the dyes.

3.2.5. Kinetic study

The adsorption kinetics of MB and CV over SDS/AC was studied by applying pseudo-first-order and pseudo-second-order kinetic models. The pseudo-second-order kinetics equation provided a better fit to the adsorption data as compared with pseudo-first-order. The pseudo-second-order kinetic parameters are given in Table 2. It is

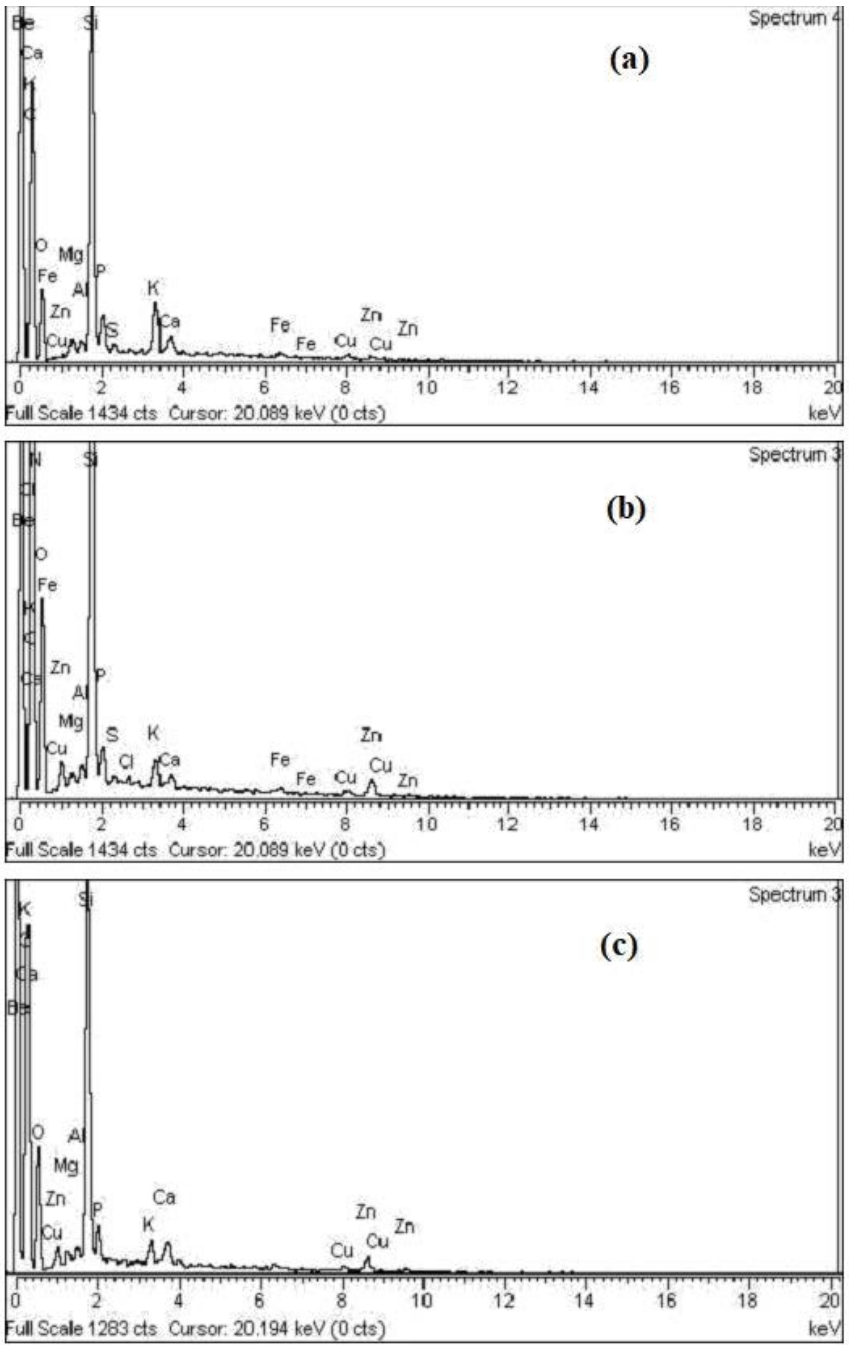

Fig. 5. Energy-dispersive X-ray spectrum (EDX) of (a) AC, (b) SDC/AC and (c) SCA/AC.

clear from the data that the adsorption of both MB and CV given straight plots with the regression factor R^2 values equal to 1, which show the accuracy of the analyzed data. Furthermore, the values of experimental and calculated q_e are in close agreement. These results clearly indicate that the adsorption of both dyes, that is, MB and CV over SDS/AC follow pseudo second order kinetics.

The adsorption data was also analyzed by intra particle diffusion kinetic model. The data from the table (Table 3) about the regression factor and reaction rate is very accurate accordingly; however, the data manipulation via pseudo second order is more reliable and thus shows the best fitting of data via pseudo-second-order reaction rate.

3.2.6. Thermodynamic parameters

For adsorption of MB and CV using 50 mg/L solution, over SDS/AC, various thermodynamic parameters were studied at different temperatures, that is, 303, 308 and 313 K. The following Eqs. (5) and (6) were used to calculate $\Delta H°$, $\Delta S°$ and $\Delta G°$.

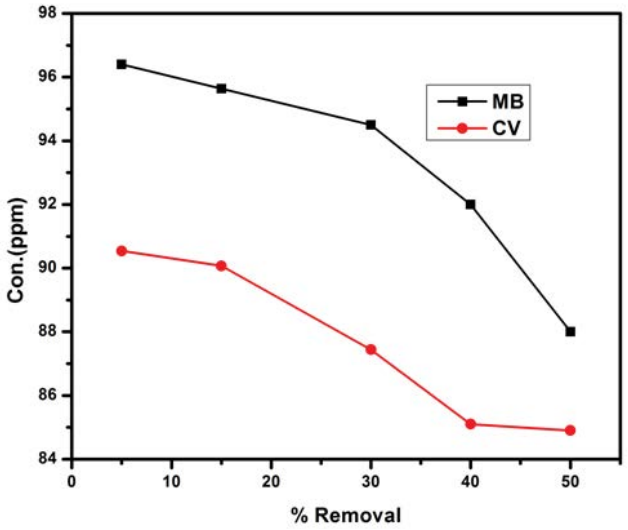

Fig. 6. Effect of initial concentration on % removal of CV and MB dyes over.

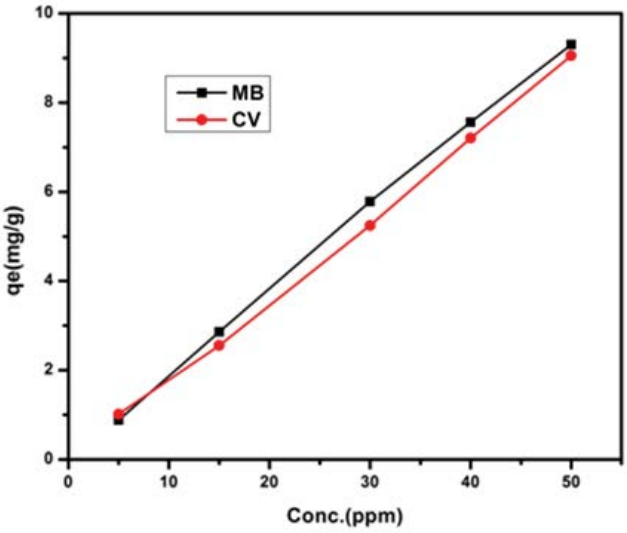

Fig. 8. Adsorption capacity q_e (mg/g) of SDS/AC for MB and CV dyes.

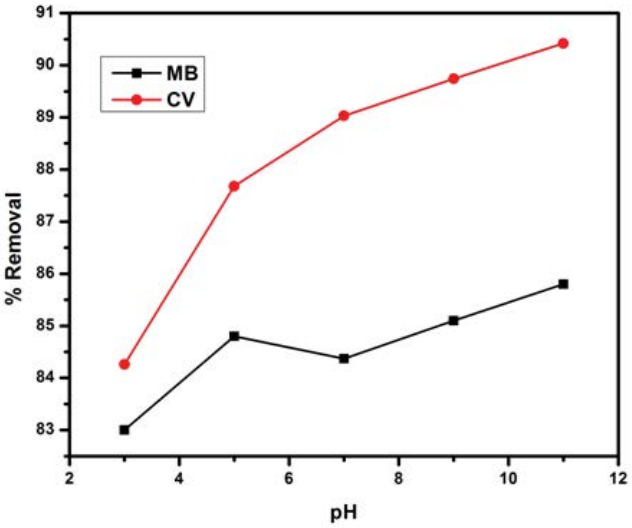

Fig. 7. Effect of pH on the removal of CV and MB by SDS AC, adjusted the pH by 0.1 N HCL and 0.1 M NaOH solution, volume of solution 40 mL, dose vale 0.5 g.

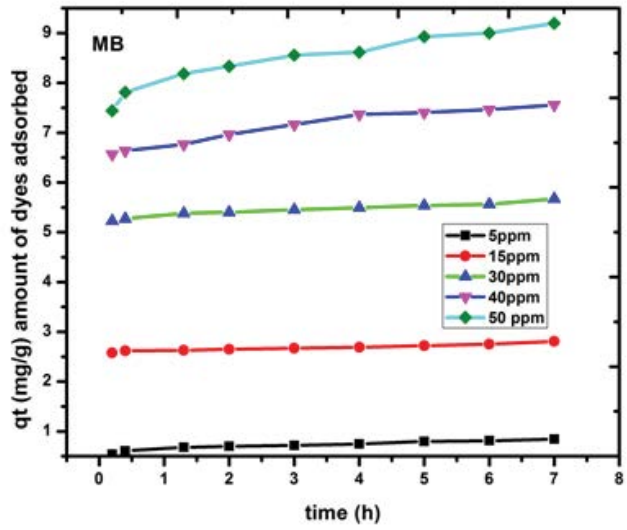

Fig. 9. Effect contact time on removal of MB over SDS/AC.

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{5}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{6}$$

where K is the equilibrium thermo dynamical constant, R is gas constant (8.314 kJ/mol), ΔS° is standard entropy change, ΔH° is standard enthalpy change and ΔG° is standard Gibbs free energy change of the process. The entropy and enthalpy were calculated from intercept and slope of the plot, plotted between $\ln K$ vs. $1/T$ (K). The enthalpy value for both CV and MB show that the process is endothermic and high temperature will favor the rate of adsorption, which was also reported in the literature [50]. Furthermore, the values of enthalpy changes show that the adsorption of dyes on the SDS/AC is physisorption phenomena (Table 4). Similarly, the positive values of entropy change in case of both CV and MB indicates that the entropy value was increased due to adsorption of the process. The value of ΔG° is negative in case of both dyes, which indicates that the adsorption process is spontaneous.

3.2.7. Isotherm study

In order to investigate nature of the adsorption process, the adsorption data was interpreted by Langmuir and Freundlich isotherms models. In case of Freundlich isotherms model, the plot was drawn between $\log q_e$ vs. $\ln C_e$, while the value of n and K_f were calculated from slope and

intercept of the graph. The regression factor of both MB and CV by Freundlich is greater than the n value which is greater than 1 for MB and less than one for CV, indicated that the process is effective.

In case of Langmuir model, the graph was plotted between C_e/q_e vs. C_e, while the constant q_{max} and b were obtained from slope and intercept of the graph. The regression factor of Langmuir model in a comparison to Freundlich is small therefore it may be assumed that the adsorption mechanism was preceded via Freundlich isotherms in both CV and MB (Table 5) which were firmly identified with Freundlich model parameters in other studies [18,19].

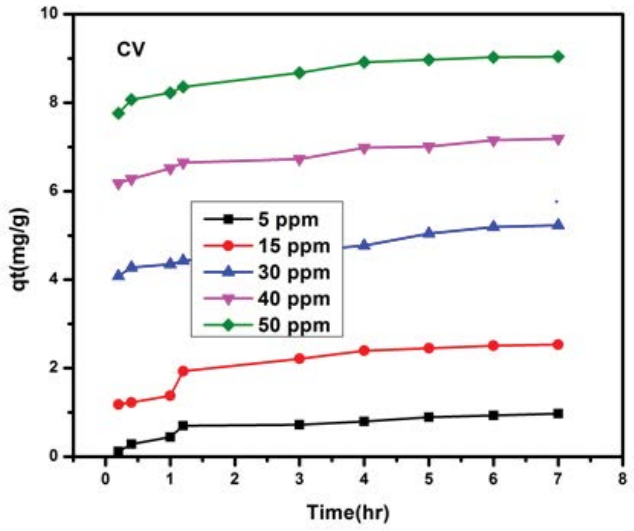

Fig. 10. Effect contact time on removal of CV over SDS/AC.

3.3. Comparison of adsorption potential of different adsorbents

The maximum adsorption capacity (q_e) of the SDS/AC adsorbent for CV and MB is compared with different adsorbents reported in the literature for MB and CV adsorption systems, as shown in Table 6.

4. Conclusion

In the present work, agriculture waste as risk husk was successfully utilized in synthesizing of AC by economic and simple method. The AC was successfully synthesized by carbonization followed by $ZnCl_2$ activation. The AC was further modified by SDS and SCA surfactants. The adsorption of MB and CV dyes were investigated over AC, SDS/AC and SCA/AC, results indicated that SDS/AC showed highest adsorption for both the dyes, under preliminary conditions. SAS, FT-IR and SEM were employed to characterize Its specific surface area, total pore volume, average pore radius, functional groups and surface morphology.

Table 2
Pseudo-second-order kinetic parameters for adsorption of MB and CV over SDS/AC

Concentration (mg/L)	MB					CV				
	5	15	30	40	50	5	15	30	40	50
Experimental q_e (mg/g)	0.880	2.860	5.780	7.560	9.300	1.015	2.554	5.246	7.205	9.054
Calculated q_e (mg/g)	0.877	2.860	5.782	7.560	9.300	0.985	2.555	5.270	7.216	9.053
K_2 (mg/g min)	3.520	5.120	1.148	1.191	0.750	0.680	0.606	0.793	1.190	1.110
R^2	0.993	0.998	0.998	0.999	0.998	0.983	0.984	0.995	0.999	0.999

Table 3
Intraparticle diffusion parameters for adsorption of MB on SDS/AC

Concentration (mg/L)	MB					CV				
	5	15	30	40	50	5	15	30	40	50
C (mg/g)	0.516	2.530	5.150	6.300	7.200	0.049	0.832	3.800	5.980	7.600
K_i (mg/g min$^{1/2}$)	0.122	0.088	0.178	0.477	0.726	0.359	0.696	0.522	0.461	0.538
R^2	0.967	0.906	0.967	0.977	0.976	0.940	0.930	0.950	0.998	0.960

Table 4
Thermodynamics parameters for adsorption MB and CV over SDS/AC

Dye	$\Delta S°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta G°$ (kJ/mol)			R^2
			30 K	308 K	313 K	
Methylene blue	0.041	10.927	–1.451	–1.693	–1.903	0.990
Crystal violet	0.111	33.270	–0.510	–1.070	–1.620	0.850

Table 5
Isotherms parameters for MB and CV dye

	Langmuir isotherm model			Freundlich isotherm model		
Dye	K_L	Q_m (mg/g)	R^2	K_f	n	R^2
Methylene blue	0.375	13.33	0.90	1.716	1.20	0.990
Crystal violet	9.2	0.103	0.81	1.0162	0.75	0.970

Table 6
Comparison of the maximum adsorption of CV and MB from this study with different various adsorbents at 25°C, pH = 9 adjusted by 0.1 N NaOH, volume of solution is 40 mL, dose 0.1 g

Dye	Adsorbent	q_e (mg/g)	Reference
	SDS/AC	9.04	Present study
CV	Palm kernel fiber	78.9	[51]
	Neem sawdust	3.8	[52]
	Sugarcane dust	3.8	[53]
	Wood apple	19.2	[54]
	Pinus bark powder	32.8	[55]
MB	SDS/AC	9.53	Present study
	Palm kernel fiber	95.4	[51]
	Activated carbon from almond shell	1.3	[56]
	Activated carbon from apricot stones	4.1	[56]
	Activated carbon from hazelnut shell	8.8	[56]
	Activated carbon (coir pith)	5.8	[57]

The adsorption process was totally depended on pH, contact time, adsorbent dosage and dye initial concentrations. The optimum conditions for maximum adsorption of both MB and CV over SDS/AC were found to be better as compared to be AC and SCA/AC, under which maximum adsorption of MB and CV over SDS/AC was found to be 90% and 85%, respectively. Kinetic studies showed that adsorption of both dyes over SDS/AC pseudo second order kinetics. The adsorption data was found to be best fitted in Freundlich for both dyes. The various thermodynamics parameters like $\Delta G°$, $\Delta H°$ and $\Delta S°$ indicated that the adsorption process is endothermic and spontaneous in nature. The maximum adsorption capacity (q_e mg/g) of SDS/AC for MB and CV was found to be by adsorbent was 9.3 mg/g for MB and 9.054 mg/g for CV from 50 mg/L solution. This shows that SDS modified AC is very efficient adsorbent for removal of MB and CV dyes from wastewater.

References

[1] J. Gupta, Driving Forces in Global Fresh Water Governance. Water Policy Entrepreneurs. A Research Companion to Water Transitions Around the Globe, Edward Elgar, Cheltenham, UK, 2009, pp. 37–60.

[2] T.M. Egan, S. Murray, R.T. Bustami, T.H. Shearon, K.P. McCullough, L.B. Edwards, M.A. Coke, E.R. Garrity, S.C. Sweet, D.A. Heiney, F.L. Grover, Development of the new lung allocation system in the United States, Am. J. Transplant., 6 (2006) 1212–1227.

[3] G. Goel, S. Kaur, A study on chemical contamination of water due to household laundry detergents, J. Hum. Ecol., 38 (2012) 65–69.

[4] C.E.L. Pereira, T.G. Heck, P.H.N. Saldiva, C.R. Rhoden, Ambient particulate air pollution from vehicles promotes lipid peroxidation and inflammatory responses in rat lung, Braz. J. Med. Biol. Res., 40 (2007) 1353–1359.

[5] A.E. Evans, J. Mateo-Sagasta, M. Qadir, E. Boelee, A. Ippolito, Agricultural water pollution: key knowledge gaps and research needs, Curr. Opin. Environ. Sustain., 36 (2019) 20–27.

[6] X. Tian, S. Chen, J. Xu, Environmental regulation, path dependence and distribution of water pollution industries: an empirical analysis based on the Yangtze River Basin, Beijing Da Xue Xue Bao, 56 (2020) 352–364.

[7] M. Samuel, B.D. Brooke, S.V. Oliver, Effects of inorganic fertilizer on larval development, adult longevity and insecticide susceptibility in the malaria vector Anopheles arabiensis (Diptera: Culicidae), Pest Manage. Sci., 76 (2020) 1560–1568.

[8] S. Singh, K.C. Barick, D. Bahadur, Functional oxide nanomaterials and nanocomposites for the removal of heavy metals and dyes, Nanomater. Nanotechnol., 3(Godište 2013) (2013) 3–20.

[9] D. Kar, P. Sur, S.K. Mandai, T. Saha, R.K. Kole, Assessment of heavy metal pollution in surface water, Int. J. Environ. Sci. Technol., 5 (2008) 119–124.

[10] R. Kant, Textile dyeing industry an environmental hazard, Nat. Sci., 4 (2011) 22–26.

[11] L.A. Shah, A. Haleem, M. Sayed, M. Siddiq, Synthesis of sensitive hybrid polymer microgels for catalytic reduction of organic pollutants, J. Environ. Chem. Eng., 4 (2016) 3492–3497.

[12] T. Wu, T. Lin, J. Zhao, H. Hidaka, N. Serpone, TiO_2-assisted photodegradation of dyes. 9. Photooxidation of a squarylium cyanine dye in aqueous dispersions under visible light irradiation, Environ. Sci. Technol., 33 (1999) 1379–1387.

[13] M.F.R. Pereira, F.S. Samanta, J.J. Órfão, J.L. Figueiredo, Adsorption of dyes on activated carbons: influence of surface chemical groups, Carbon, 41 (2003) 811–821.

[14] S. Tian, S. Xu, J. Liu, C. He, Y. Xiong, P. Feng, Highly efficient removal of both cationic and anionic dyes from wastewater

with a water-stable and eco-friendly Fe-MOF via host-guest encapsulation, J. Cleaner Prod., 239 (2019) 117767.
[15] S. Meriç, D. Kaptan, T. Ölmez, Color and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process, Chemosphere, 54 (2004) 435–441.
[16] H.A. Ahsaine, M. Zbair, Z. Anfar, Y. Naciri, N. El Alem, M.J.M.T.C. Ezahri, Cationic dyes adsorption onto high surface area 'almond shell' activated carbon: kinetics, equilibrium isotherms and surface statistical modeling, Mater. Today Chem., 8 (2018) 121–132.
[17] K.A. Adegoke, O.S. Bello, Dye sequestration using agricultural wastes as adsorbents, Water Resour. Ind., 12 (2015) 8–24.
[18] M. Ilyas, W. Ahmad, H. Khan, I. Ahmad, Application of composite adsorbents prepared from waste PS and PET for removal of Cr and Cu ions from wastewater, Desal. Water Treat., 171 (2019) 144–157.
[19] M. Ilyas, W. Ahmad, H. Khan, S. Yousaf, Potentially poisonous elements removal from vehicle-wash wastewater and aqueous solutions using composite adsorbents, Desal. Water Treat., 224 (2021) 331–342.
[20] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, J. Hazard. Mater., 97 (2003) 219–243.
[21] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, Adsorption of methylene blue on low-cost adsorbents: a review, J. Hazard. Mater., 177 (2010) 70–80.
[22] J. Maity, S.K. Ray, Chitosan based nano composite adsorbent—synthesis, characterization and application for adsorption of binary mixtures of Pb(II) and Cd(II) from water, Carbohydr. Polym., 182 (2018) 159–171.
[23] S. Sivakumar, P. Senthilkumar, V. Subburam, Carbon from cassava peel, an agricultural waste, as an adsorbent in the removal of dyes and metal ions from aqueous solution, Bioresour. Technol., 80 (2001) 233–235.
[24] F. Ferrero, Dye removal by low cost adsorbents: hazelnut shells in comparison with wood sawdust, J. Hazard. Mater., 142 (2007) 144–152.
[25] K.A. Krishnan, K.G. Sreejalekshmi, R.S. Baiju, Nickel(II) adsorption onto biomass based activated carbon obtained from sugarcane bagasse pith, Bioresour. Technol., 102 (2011) 10239–10247.
[26] M. Naushad, A.A. Alqadami, Z.A. AlOthman, I.H. Alsohaimi, M.S. Algamdi, A.M. Aldawsari, Adsorption kinetics, isotherm and reusability studies for the removal of cationic dye from aqueous medium using arginine modified activated carbon, J. Mol. Liq., 293 (2019) 111442.
[27] A.F. Streit, L.N. Côrtes, S.P. Druzian, M. Godinho, G.C. Collazzo, D. Perondi, G.L. Dotto, Development of high quality activated carbon from biological sludge and its application for dyes removal from aqueous solutions, Sci. Total Environ., 660 (2019) 277–287.
[28] A.M.A. Ali, R.K. Karthikeyan, S.M. Sentamil, M.K. Rai, M. Priyadharshini, V.C. Padmanaban, R.S. Singh, Removal of Reactive Orange 16 by adsorption onto activated carbon prepared from rice husk ash: statistical modelling and adsorption kinetics, Sep. Sci. Technol., 55 (2020) 26–34.
[29] Altıntıg, H. Altundag, M. Tuzen, A. Sarı, Effective removal of methylene blue from aqueous solutions using magnetic loaded activated carbon as novel adsorbent, Chem. Eng. Res. Des., 122 (2017) 151–163.
[30] Altıntıg, M. Yenigun, A. Sarı, H. Altundag, M. Tuzen, T.A. Saleh, Facile synthesis of zinc oxide nanoparticles loaded activated carbon as an eco-friendly adsorbent for ultra-removal of malachite green from water, Environ. Technol. Innovation, 21 (2021) 101305.
[31] T.A. Saleh, S.H. Al-Ruwayshid, A. Sarı, M. Tuzen, Synthesis of silica nanoparticles grafted with copolymer of acrylic acrylamide for ultra-removal of methylene blue from aquatic solutions, Eur. Polym. J., 130 (2020) 109698.
[32] E. Altintig, M. Onaran, A. Sarı, H. Altundag, M. Tuzen, Preparation, characterization and evaluation of bio-based magnetic activated carbon for effective adsorption of malachite green from aqueous solution, Mater. Chem. Phys., 220 (2018) 313–321.
[33] M. Tuzen, A. Sarı, T.A. Saleh, Response surface optimization, kinetic and thermodynamic studies for effective removal of rhodamine B by magnetic AC/CeO_2 nanocomposite, J. Environ. Manage., 206 (2018) 170–177.
[34] S.M. Wabaidur, M.A. Khan, M.R. Siddiqui, Z.A. ALOthman, M.S. Al-Ghamdi, H.I. Al-Sohami, Dodecyl sulfate chain anchored bio-char to sequester triaryl methane dyes: equilibrium, kinetics, and adsorption mechanism, Desal. Water Treat., 67 (2017) 357–370.
[35] A. Aldawsari, M.A. Khan, B.H. Hameed, Z.A. ALOthman, M.R. Siddiqui, Y.B.H. Ahmed, I.H. Alsohaimi, Development of activated carbon from *Phoenix dactylifera* fruit pits: process optimization, characterization, and methylene blue adsorption, Desal. Water Treat., 62 (2017) 273–281.
[36] M. Yusuf, M.A. Khan, E.C. Abdullah, M. Elfghi, M, Hosomi, A. Terada, S. Riya, A. Ahmad, Dodecyl sulfate chain anchored mesoporous graphene: synthesis and application to sequester heavy metal ions from aqueous phase, Chem. Eng. J., 304 (2016) 431–439.
[37] S.A. Alshareef, M. Otero, H.S. Alanazi, M.R. Siddiqui, M.A. Khan, Z.A. ALOthman, Upcycling olive oil cake through wet torrefaction to produce hydrochar for water decontamination, Chem. Eng. Res. Des., 170 (2021) 13–22.
[38] M.A. Khan, R. Govindasamy, A. Ahmad, M.R. Siddiqui, S.A. Alshareef, A.A.H. Hakami, M. Rafatullah, Carbon based polymeric nanocomposites for dye adsorption: synthesis, characterization, and application, Polymers, 13 (2021) 419.
[39] S.M. Wabaidur, M.A. Khan, M.R. Siddiqui, M. Otero, B.H. Jeon, Z.A. ALOthman, A.A.H. Hakami, Oxygenated functionalities enriched MWCNTs decorated with silica coated spinel ferrite–a nanocomposite for potentially rapid and efficient de-colorization of aquatic environment, J. Mol. Liq., 317 (2020) 113916.
[40] M.A. Khan, M.R. Siddiqui, M. Otero, S.A. Alshareef, M. Rafatullah, Removal of Rhodamine B from water using a solvent impregnated polymeric dowex 5wx8 resin: statistical optimization and batch adsorption studies, Polymers, 12 (2020) 500.
[41] M.A. Khan, M. Otero, M. Kazi, A.A. Alqadami, S.M. Wabaidur, M.R. Siddiqui, Z.A. ALOthman, S. Sumbul, Unary and binary adsorption studies of lead and malachite green onto a nanomagnetic copper ferrite/drumstick pod biomass composite, J. Hazard. Mater., 365 (2019) 759–770.
[42] E.R. Kenawy, A.A. Ghfar, S.M. Wabaidur, M.A. Khan, M.R. Siddiqui, Z.A. ALOthman, A.A. Alqadami, M. Hamid, Cetyltrimethylammonium bromide intercalated and branched polyhydroxystyrene functionalized montmorillonite clay to sequester cationic dyes, J. Environ. Manage., 219 (2018) 285–293.
[43] W. Li, L.B. Zhang, J.H. Peng, N. Li, X.Y. Zhu, Preparation of high surface area activated carbons from tobacco stems with K_2CO_3 activation using microwave radiation, Ind. Crops Prod., 27 (2008) 341–347.
[44] Y. Guo, J. Qi, S. Yang, K. Yu, Z. Wang, H. Xu, Adsorption of Cr(VI) on micro-and mesoporous rice husk-based active carbon, Mater. Chem. Phys., 78 (2003) 132–137.
[45] M. Li, S.K. Cushing, X. Zhou, S. Guo, N. Wu, Fingerprinting photoluminescence of functional groups in graphene oxide, J. Mater. Chem., 22 (2012) 23374–23379.
[46] R.N. Oliveira, M.C. Mancini, F.C.S.D. Oliveira, T.M. Passos, B. Quilty, R.M.D.S.M. Thiré, G.B. McGuinness, FTIR analysis and quantification of phenols and flavonoids of five commercially available plants extracts used in wound healing, Matéria (Rio de Janeiro), 21 (2016) 767–779.
[47] S. Sharma, C. Nirkhe, S. Pethkar, A.A. Athawale, Chloroform vapour sensor based on copper/polyaniline nanocomposite, Sens. Actuators, B, 85 (2002) 131–136.
[48] M. Erdem, R. Orhan, M. Şahin, E. Aydın, Preparation and characterization of a novel activated carbon from vine shoots by $ZnCl_2$ activation and investigation of its rifampicine removal capability, Water Air Soil Pollut., 227 (2016) 226.

[49] T.U. Rehman, L.A. Shah, M. Khan, M. Irfan, N.S. Khattak, Zwitterionic superabsorbent polymer hydrogels for efficient and selective removal of organic dyes, RSC Adv., 9 (2019) 18565–18577.
[50] T.U. Rehman, S. Bibi, M. Khan, I. Ali, L.A. Shah, A. Khan, M. Ateeq, Fabrication of stable superabsorbent hydrogels for successful removal of crystal violet from waste water, RSC Adv., 9 (2019) 40051–40061.
[51] G.O. El-Sayed, Removal of methylene blue and crystal violet from aqueous solutions by palm kernel fiber, Desalination, 272 (2011) 225–232.
[52] S.D. Khattri, M.K. Singh, Colour removal from synthetic dye wastewater using a bioadsorbent, Water Air Soil Pollut., 120 (2000) 283–294.
[53] R. Kumar, R. Ahmad, Biosorption of hazardous crystal violet dye from aqueous solution onto treated ginger waste (TGW), Desalination, 265 (2011) 112–118.
[54] S.D. Khattri, M.K. Singh, Colour removal from dye wastewater using sugar cane dust as an adsorbent, Adsorpt. Sci. Technol., 17 (1999) 269–282.
[55] R. Ahmad, Studies on adsorption of crystal violet dye from aqueous solution onto coniferous pinus bark powder (CPBP), J. Hazard. Mater., 171 (2009) 767–773.
[56] A. Aygun, S. Yenisoy-Karakas, I. Duman, Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties, Microporous Mesoporous Mater., 66 (2003) 189–195.
[57] D. Kavitha, C. Namasivayam, Experimental and kinetic studies on methylene blue adsorption by coir pith carbon, Bioresour. Technol., 98 (2007) 14–21.