Surface Modification of Adsorbent Using Basic Activating Agent For Removal of Anionic and Cationic Dyes

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Abstract

Surface modification of adsorbents is crucial in improving adsorption behaviour and adsorption capacity/selectivity. In the present study, surface modification of commercial Norit PK (3-5) for the removal of anionic dye Congo red (CR) and cationic dye Brilliant Green (BG) was studied. The modification chosen on Norit is base modification (BM) using activating agent. The adsorption of the dyes on the modified adsorbent was compared with the unmodified Norit (UN). Characterization of the adsorbents was carried 38out using SEM, EDX, TEM, FTIR for detailing surface characteristics and BET for surface area/ pore size analysis. The extent of removal of dye on the adsorbent was studied experimentally and by studying isotherms of the adsorption system. Batch adsorption was conducted out by varying dosage of adsorbents, contact time and initial concentration of dyes. The equilibrium data was analysed using two adsorption isotherm models; Langmuir and Freundlich. It was observed that the modification provides significant improvement and the modified adsorbent can be used prominently for removal of anionic and cationic dyes because of the improved adsorption behaviour compared to unmodified adsorbent.

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Key words: Adsorption, Surface modification, Dyes, activated carbon, wastewater treatment.

1. Introduction

A dye is a colored substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution and it is a chemical which on binding on material gives a color to it. There are more than 100,000 commercially available dyes with over 7×10^5 tons of dye stuff are produced annually. Dye contaminated effluents, in large volumes, get generated from industries such as textile, paper and pulps, plastics, leather, food and cosmetics industries[1]. Many of the dyes are harmful, impart colour to the effluents and therefore the effluent needs to be treated for the removal of dyes prior to the discharge in the surface waters. Many a times, the colour is imparted even when the concentration of the dye is very low and here the adsorptive removal of the dyes is largely promising operation and is commonly practiced.

There exist several methods for dye removal such as coagulation and flocculation, oxidation, cavitation, ozonation and membrane separation. Some of the removal methods, e.g. adsorption, coagulation, membranes, generate secondary waste whereas oxidative methods such as cavitation largely destroy the polluting species resulting in mineralization and therefore are considered as destructive technologies compared to removal technologies. Further, the technologies such as membranes are cost intensive and typically have techno-economic disadvantages. Adsorption is a well - established method for removal of dyes from aqueous solution. Adsorption method does not require high temperature environment; it is simple to design and easy to operate[2,3]. Hundreds of adsorbents have been reported for the removal of dyes, from natural resources to synthetic adsorbents. Surface characteristics are crucial for selective removal of the dyes and hence modification if the adsorbents can provide improvements in the adsorption behaviour, in terms of increased capacity or rates of adsorption, thereby positively altering the viability of the commercial application.

Different types of adsorbents such as activated carbon, silica, zeolites peat, chitin, and others have been reported in literature for removal of dyes[4]. The adsorbent is the separating agent used to express the difference between molecules in a mixture: adsorption equilibrium or kinetics. An adsorbent is a substance, usually porous in nature and with a high surface area that can attach substances onto its surface by different forces such as strong electrostatic attraction, or weak van der Waal forces. Activated carbon is the most

commonly used adsorbent to remove various molecules from water or gases and is known for its useful adsorption capacity, surface area, structure and many physical or chemical modification possibilities with high degree of surface[5]. Activated carbons from carbonaceous materials can be prepared in two steps: the carbonization and the activation of carbonized product, with or without further modifications. The purpose of carbonization is to remove moisture in order to create an initial porosity. Activation process helps to define the material characteristics such as pore size, tortuosity etc. It can be carried out by chemical or physical methods. In physical activation, the material is first carbonized in an inert atmosphere then it is activated using oxidizing agents such as steam or carbon dioxide; whereas in chemical activation, material is impregnated with activating agent such as zinc chloride ($ZnCl_2$), potassium hydroxide (KOH) or phosphoric acid (H_3PO_4) and carbonized in an inert atmosphere. The important characteristic of an activated carbon includes its adsorption capacity, selectivity which depends on the nature of the material as well as on the manufacturing process[6].

Among the various commercial adsorbents, Norit is one common carbon-based adsorbent known for its good adsorption properties. Norit adsorbent has been used for cleanup of chlorinated pesticides by Richard A. Baetz[7]. The adsorbent was useful for a rapid cleanup in order to determine 13 pesticides at levels of 0.1 to 1 ppm to be analysed by Gas Chromatography. Santos *et al.*[8] studied the comparison between a developed adsorbent with Norit in the adsorption of drugs such as acetaminophen and diclofenac. The adsorption capacity of the developed adsorbent was found to be higher than Norit. Dimya and Potangale[9] have studied the comparison of adsorption capacity of chitosan and activated charcoal for nickel ions. It was observed that capacity of chitosan was 67 times higher than activated charcoal.

In the present study, a commercially available activated carbon (Norit PK 3-5) has been evaluated for removal of anionic (Congo Red) and cationic dyes (Brilliant Green). The aim of present study is to investigate the effect of activating agents on the adsorption capacity of modified Norit.

2. Experimental

Norit PK 3-5 (mesh size 4-14), Congo Red (CR) and Brilliant Green (BG) dyes were purchased from Sigma-Aldrich, ammonia (NH_3) and potassium hydroxide (KOH) of analytical grade were purchased from Loba Chemie.

A stock solution of 1000 ppm of each dye was prepared by dissolving accurately weighed sample in 1 L of distilled water. Serial dilution was done for preparation of desired lower concentrations. Synthetic dye mix was standardized by measuring the absorbance of various concentrations of the dye solution at 696 for CR and 625 nm for BR using spectrophotometer.

2.1 Analytical

The absorbance of the dye solution was determined using UV spectrophotometer (Hitachi U-2800). An advanced Scanning Electron Microscope (SEM) (JEOL JSM-6480 LV) attached with Energy Dispersive X-ray spectroscopy (EDX) (Bruker, Quanrax-200, Berlin, Germany) with automated gas sorption system for N_2 adsorption isotherm was used for the analysis of morphology and chemical composition of the adsorbents. TEM (JEOL Ltd) was used to characterize the structure and morphology of the adsorbents. Surface functional groups on the modified adsorbents were determined by Cary 600 FT-IR (Agilent) spectrophotometer having 4 cm^{-1} resolution using KBr pellet method in the range 400-4000 cm^{-1}. The surface area of the adsorbents was measured using BET (Quantachrome (Autosorb)).

2.2 Surface modification of adsorbent- Norit

Selective activating agents such as ammonia and potassium hydroxide were used for the preparation of base-modification form of Norit**.** A known quantity, 40 g, of Norit was heated in a muffle furnace at 300 °C for 3 h. A required volume of ammonia was gradually added with continuous stirring. The sample was then dried in oven at 110 °C for 24 h. It was washed with distilled water until it was free of ammonia and was dried. Potassium hydroxide was added in the ratio of 1:1 w/w and was heated at 70 °C with continuous stirring for 1 h. The mixture was then carbonized in a horizontal tubular furnace at 300 °C under continuous nitrogen flow at a rate of 75 mL/min for 3 h. The carbonized material was treated with 1 M hydrochloric acid, subsequently washed with distilled water until free of chloride ions. The sample was finally dried and was employed in the studies.

2.3 Adsorption studies

For batch adsorption studies, a known quantity of the adsorbent (e.g. 0.1 g of adsorbent) was added to a known volume (e.g. 20 mL) of predetermined concentration of (e.g. 200 ppm) dye solution to a conical flask. The mixture was agitated for 3 h at ambient temperature at 130 rpm until equilibrium was achieved using orbital shaker (Spectralab HM8T). The adsorbent was separated from solution by filtration using Whatman No.41 filter paper. The effect of dosage, contact time and initial dye concentration was evaluated. The reduction in colour of the solution or un-adsorbed dye was measured by UV spectrophotometer to study the percentage adsorption. The quantity of dye adsorbed at given time *t* and the percentage removal of dye was calculated using eq. (1).

$$\%R = \frac{(c_o - c_e)}{c_o} \times 100 \qquad (1)$$

Where C_0 is the initial and *Ce* is the equilibrium concentrations of the dye in mg/L.

3. Results and Discussion

3.1 Characterization

SEM analysis is used to study the morphology features and surface characterisation of adsorbent. Fig.1 shows change in morphology after basic activating agent was applied to Unmodified Norit adsorbent, (UN). Base modification adsorbent (BM) (Fig. 1(a)) shows irregular surface with pores of different sizes while the surface of UN depicts sharp edges with micropores.

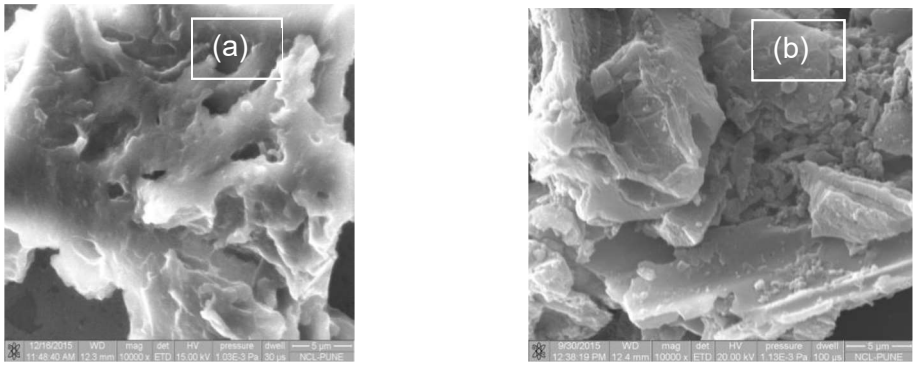

Fig. 1. SEM images of (a) BM (b) UN

The EDX spectrum allows accurate identification of the chemical elements present in the adsorbent. It identifies the essential components of the backbone which are carbon and oxygen of the structure of the adsorbents (Table 1). Si, Fe, K, Ca, Cu and Mn were also

present in low concentrations which may be detected in the activating agent and in impurities.

TEM allows to view the fundamental structure of the functional materials. The micrographs of the adsorbents (Fig. 2) show agglomerated “rod-like” structures for BM (Fig. 2(a)) on the backbone of UN (Fig. 2(b)).

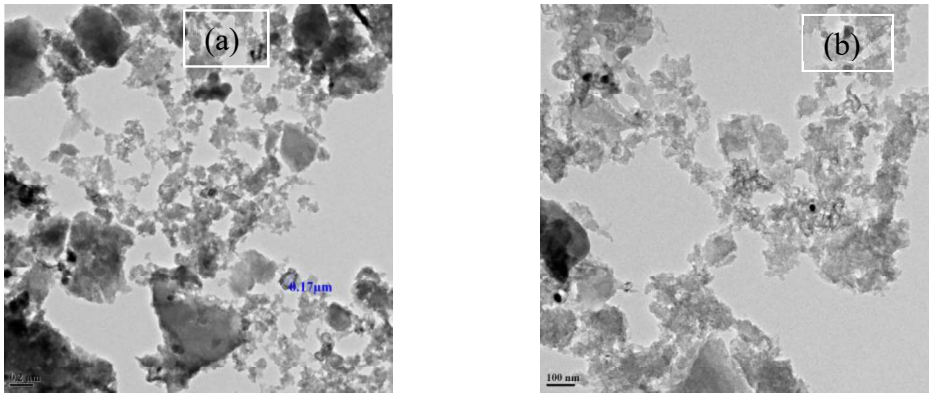

Fig. 2. TEM images (a) BM (b) UN

FT-IR analysis permits spectrophotometric observation of the adsorbent surface in the range of 400-4000 cm^{-1} and indicated the organic functional groups on the surface of the adsorbents. IR spectra (Fig. 3(a)) shows a peak at band at 1162 cm^{-1} indicating presence of C-O stretching bond followed by peak at 1375 cm^{-1} - corresponds to the presence of C-H bending (alkenes). The band at 1700 cm^{-1} may be assigned for C=O with a prominent peak. In Fig. 3(b), the peak observed at 1104 cm^{-1} may be due to presence of C-N stretching of aliphatic amines and 1372 cm^{-1} is due to strong stretching. The band range 1600 -1500 cm^{-1} is due to C=C stretching in presence of aromatic compound[10].

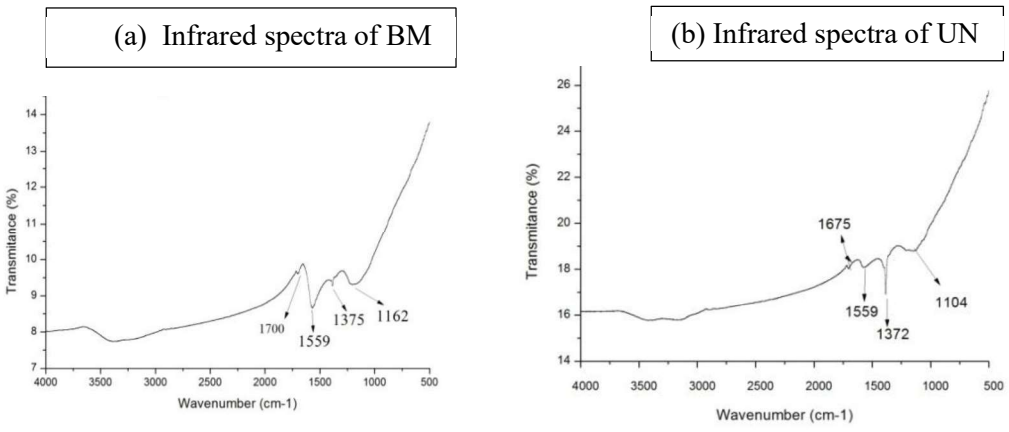

Fig. 3. FT-IR spectra of (a) BM (b) UN

The measurements for surface area were done on a Bruner-Emmett-Teller (BET) instrument. Table 1 shows the analysis of BM and UN for surface area (m^2/g) and for average pore diameter (nm). It is can be concluded that after the base modification of UN, the surface area of BM increased as well as the average pore diameter. After modification, surface area decreases but average pore diameter increases which may suggest an increase in adsorption capacity due to the presence of active sites.

Table 1: Atomic weight in percentage of elemental compositions, surface area and porosity of adsorbents

Properties	BM	UN
Elemental	39.07 of C	64.71 of C
	13.01 of O	16.96 of O
BET Surface area (m^2g^{-1})	699.00	699.00
Average pore diameter (nm)	0.3123	0.3123

3.2 Adsorption studies

3.2.1 Effect of adsorbent dosage

The influence of adsorbent dosage on decolourisation of the dyes was studied from 0.1 – 1 g while maintaining 20 mL of 200 ppm of dye solution with continuous shaking for 6 h at 130 rpm to ensure equilibrium. The percentage of dye removal increased with the adsorbent dosage. More than 98% dye removal of CR and BG was observed by the adsorbents. This can be attributed to the possibility of adsorption sites become available at an increasing rate with an increase in the adsorbent's surface area.

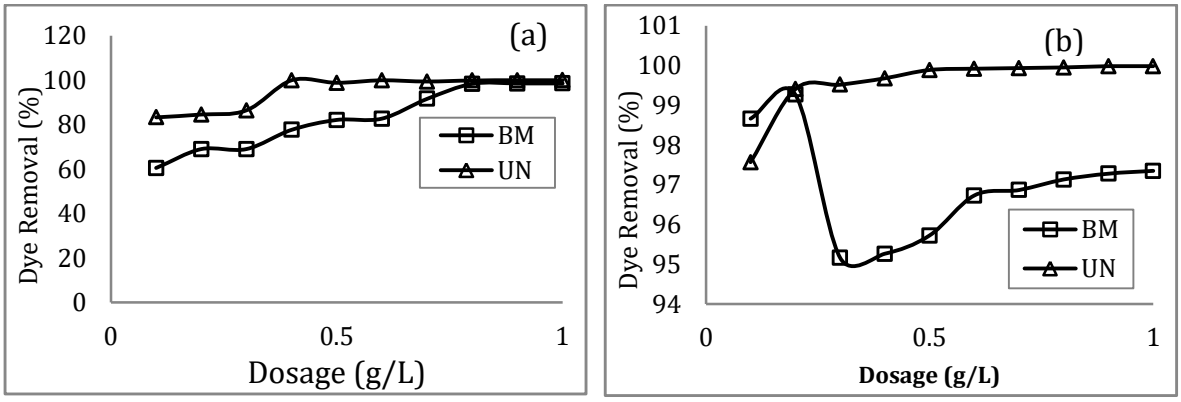

Fig. 4. Effect of dosage of adsorbents for (a) CR and (b) BG

3.2.2 Effect of Agitation time

The effect of agitation time on dye removal is studied and it is observed that BM requires lesser time than UN for achieving maximum colour reduction. From Fig. 5, it is found that the optimized agitation time for decolourising CR is 1 and 3 h with BM and UN, respectively. The dye removal for BG, using BM and UN requires 1 and 4 h, respectively.

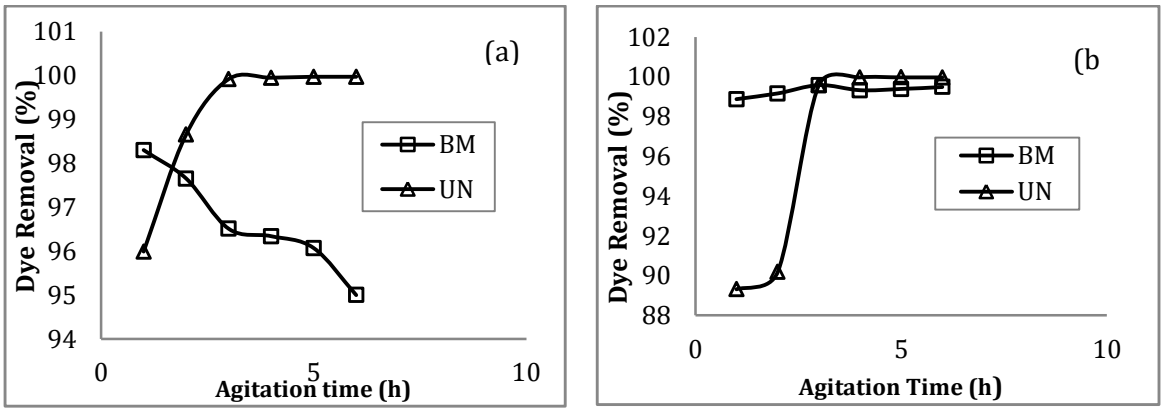

Fig. 5. Effect of agitation time for dye removalfor (a) CR and (b) BG

3.2.3 Effect of dye concentration

The effect of concentration of CR and BG was investigated and the results are shown in Fig. 6. As the concentrations of dye increased, the % dye removalalso increased for BM. However, a decrease was observed from 150 ppm in the case of UN for the adsorption of CR. This could be due the unavailability of active sites on its surface. For BG, the decrease was negligible for the adsorbents.

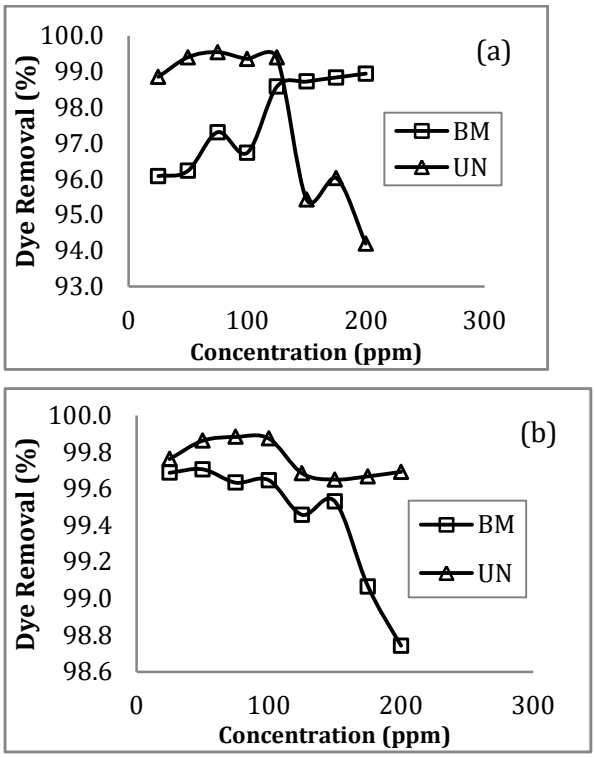

Fig. 6. Effect of concentration of (a) CR and (b) BG on colour reduction

3.3. Isotherm studies

Adsorption isotherm depicts relationship between amount of adsorbate per unit mass of adsorbent and concentration of adsorbate solution at equilibrium time[11]. Isotherms are related to the details on the mechanism of the adsorbate-adsorbent system and the adsorbent's surface properties. Hence, it is useful for calculating maximum capacity of adsorbate taken by adsorbent[12]. Two isotherm models were used to study the mechanism of adsorption.

3.3.1 Langmuir Isotherm:

The isotherm, when correctly described, either theoretically or empirically, gives an idea of the maximal adsorption capacity of the adsorbent. The primary assumption of Langmuir isotherm is the formation of monolayer of adsorbate on the surface of adsorbent and after that no further adsorption takes place as per this model[13]. The adsorption is considered to be on the surface of structurally homogeneous adsorbent, where all the sorption sites are identical and energetically equivalent[14]. The mathematical expression of Langmuir isotherm is as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m \times b} \qquad (3)$$

where C_e is the equilibrium concentration of adsorbate (mg/L); q_e the adsorption capacity (mg/g); and b and q_m are the Langmuir constants. The values of Langmuir constants b and q_m were calculated from the slope and intercept of the linear plot of Ce/qe versus Ce respectively. The coefficient b is a measure of the stability of the complex formed between the dye and the adsorbent under specified experimental conditions. A separation factor termed the equilibrium parameter, abbreviated R_L, can be used to represent the Langmuir isotherm. R_L which is expressed as (4).

$$R_L = \frac{1}{1+bC_i} \qquad (4)$$

where b is Langmuir constant and C_i is the initial dye concentration. The R_L value reveals both the isotherm's shape and the nature of the adsorption process. Adsorption is if R_L=0 it is irreversible, unfavourable if R_L value>1, favourable if 0<R_L<1. In the current investigation, the adsorption of CR is found to be favourable for UN (R_L= 0.005) only while the adsorption of BG is observed to be favourable for adsorbents BM (R_L = 0.005) and (UN R_L = 0.001).

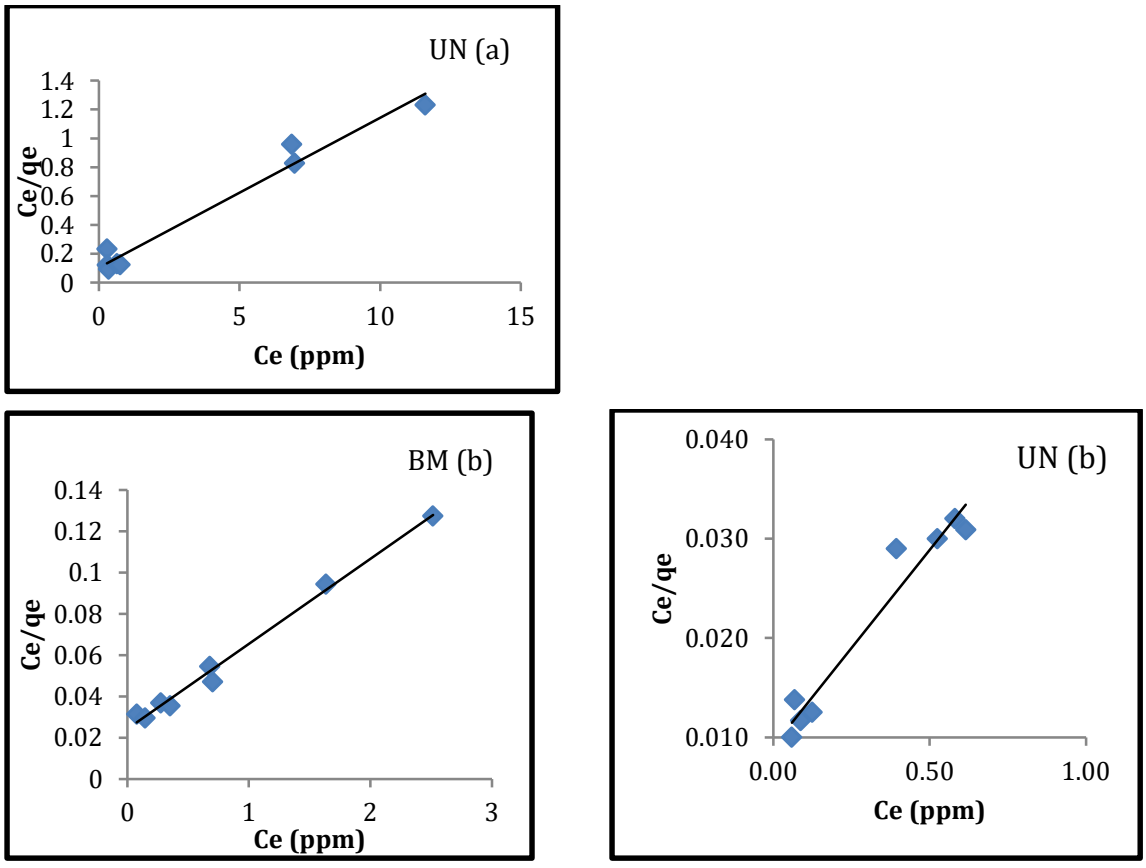

Fig. 7. Langmuir isotherm for adsorption of (a) CR on UN and (b) BG on both BM and UN

3.3.2 Freundlich Isotherm:

Freundlich isotherm describes adsorption behaviour on heterogeneous surfaces of adsorbents. It defines the surface heterogeneity and the exponential distribution of active sites and their energies. The linear form of Freundlich isotherm is as follows[15]

$$\text{Log } q_e = \frac{1}{n} \log C_e + \log K_f \qquad (4)$$

Where, q_e(mg/g) is amount of material adsorbed at equilibrium, C_e(mg/l) is equilibrium adsorbate concentration in liquid solution, K_f is Freundlich constant. If the magnitude of $1/n$ is equal to 1, the adsorption is linear. If the value is either less or more than unity, the adsorption is a chemical or physical mechanism. The parameters of Freundlich model, n and K_f are calculated from slope and intercept of plot of log q_e Vs log C_e, respectively.

Table 2: Isotherm constants for CR

Adsorbent	**q_m(mg/g)**	**b (L/mg)**	**R_L**
Langmuir Isotherm			
BM	-	-	-
UN	9.615	1.004	0.005

Table 3: Isotherm constants for BG

Adsorbent	**q_m (mg/g)**	**b (L/mg)**	**R_L**
Langmuir Isotherm			
BM	24.213	1.000	0.005
UN	25.381	4.329	0.001
Freundlich Isotherm			
	1/n		**K_f**
BM	0.575		14.534
UN	-		-

Conclusions:

The adsorption studies indicated that dye removal of CR is easier compared to BG, where the maximum reduction was observed as 99 and 20%, respectively. The SEM images show spherical particles on surface having microporous surface, pores of different sizes, cavities on surface and porous in nature. The TEM images show the structures of both the adsorbents depicting sheets forms which are responsible for high adsorption of dye. The

results of the experiment are examined using adsorption isotherm models. The equilibrium data is best explained by Langmuir and Freundlich isotherms by adsorbent BM for BG. The optimized conditions for dye removal greater than 98% of BM and UN for adsorption for CR dye are: 1 and 3 h contact time at dosages of 0.8 and 0.6 g at initial concentration of 200 and 100 ppm, respectively. For BG the optimized conditions are contact time of 2 and 3 h of dosage 0.2 g for both and initial concentration of 200 ppm for dye removal of 99%.

The data obtained for adsorption of CR do fit the models. However, the data observed for adsorption of BG by BM fits the Freundlich models (1/n = 0.575) concluding that the mechanism of adsorption of the systems could be chemical or physical. R_L is not equal to zero for both the dyes adsorption systems. Hence, this does not indicate an irreversible mechanism. These criteria conclude that the adsorption mechanisms for both dyes are physisorption[16,17].

The modified adsorbent BM appear to be a potential material for the removal of colour and useful for removal of dyes of the type CR; where it requires lesser contact time with high capacity indicating significantly reduced costs.

Authors' Contributions:

The authors have contributed equally.

Conflict of Interest:

There is no conflict of interest.

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