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Abstract

The present work investigates comparative dye [malachite green (MG)] adsorption efficiency of alginate beads (A0) and prepared composite materials of alginate [i.e., Alginate-bentonite (AB), activated carbon-alginate beads (AC), and activated carbon-bentonite-alginate beads (ABC)] from aqueous solution. Results revealed that among all the composite materials under investigation alginate-bentonite (AB) beads have maximum adsorption capacity (i.e., 69.90 mg/g) compared to others at 30°C and neutral pH. Further, all the prepared composites were characterized by conducting SEM (Scanning Electron Microscopy), FTIR (Fourier transform infrared spectroscopy) and fluorescence imaging before and after adsorption. The images obtained from SEM and fluorescence microscopy confirmed the dye adsorption by all the composite materials. The equilibrium adsorption data was fitted well to Langmuir adsorption isotherm models which confirm the monolayer adsorption behavior of dye molecules onto the surface of all the adsorbents under study. Kinetic studies revealed that dye adsorption on A0, AC, AB and ABC composite followed pseudo-second order kinetic model

Keywords: Adsorption, Alginate, Bentonite, Activated Carbon, Composite, Malachite Green

1. Introduction

Dyes are widely being used by several industries such as textile dyeing, food processing, cosmetics, paper printing pharmaceuticals etc. [1]. Among these industries, textile industries are the major consumer as well as source of discharge of different dyes in their effluent, as these textile industries lose approximately 12% of dyes while the manufacturing and dyeing processes[2]. According to Stefanakis et al., only 47% of these dyes released in textile industries effluent are biodegradable[3]. Hence, the water bodies present in the vicinity of dyeing industries are getting severely contaminated with non-biodegradable persistent dyes or color pigments which seriously threaten the aquatic ecosystem as well as human health [3], [4], [2]. Further, these non-biodegradable and toxic dyes released in water bodies may cause acute or chronic effect on aquatic organisms after entering in the food chain through water and ultimately affect the health of human beings and animals [5]. Hence, the removal/treatment of these dyes should be done to avoid the environmental consequences.

Current prospects for the dye removal involve physicochemical techniques i.e., coagulation, chemical oxidation/reduction procedure, photo- degradation, membrane filtration, adsorption [6], [7, 8]. They have been effectively applied for the removal of various dyes from mixed aqueous solutions and/or industrial wastewater. All these methods have their own pros and cons in terms of their effectiveness, cost, and environmental impact [9]. Among all the above-mentioned methods, adsorption has been reported as the commonly used technique for the removal of toxic organic and inorganic dyes as well as micro-pollutants from wastewater due to its performance and ease of operation [10].

Alginic acid polymers are widely used in many adsorption based wastewater treatment applications due to their versatile properties [11], [12], [13]. Their high bioavailability and easy extraction process make them cost-effective. Alginate is a very efficient sorbent for dyes, However, the main drawback of its use as adsorbent is the weak mechanical strength and subsequently its weak ability for repeated use. To solve this problem researcher incorporated sodium alginate in natural composite hydrogels[14]. The encapsulation of natural adsorbent, i.e. Activated carbon (AC), Bentonite clay (BC), into alginate beads is a promising solution to overcome this problem. The incorporation of natural adsorbent within an alginate matrix improves its mechanical strength and regeneration ability. The use of alginate as a carrier material for natural adsorbents has enlightened the possibility of having selective adsorption of organic molecules, depending on their electrical charge, due to interaction with the negative carboxylate groups on alginate.

Malachite Green (MG), a tri-phenyl-methane cationic dye is universally used for dyeing of textiles (cotton, silk), paper, leather, manufacturing of paints and printing inks. The MG is extremely toxic dye to mammalian cells and causes damaging effects in liver, gill, kidney, intestine, gonads, and pituitary gonadotropic cells. Moreover, it might break through the food chain and can cause carcinogenic, mutagenic and teratogenic effects on mammals. In spite of ban in several countries, the dye is still being used due to the ease of availability, cost-effectiveness, and usefulness [15]. Therefore, it is essential to treat the discharged effluent containing MG pollutions.

Therefore, the objectives of this study were as follows: first, to prepare a variety of composite beads from the combination of alginate-bentonite beads (AB), alginate beads- activated carbon (AC), and alginate beads-bentonite-activated carbon (ABC) via a simple crosslinking method; second, to compare and verify the best composite among the prepared samples; third, to evaluate the best composite as an adsorbent for the removal of the model dye Malachite Green (MG) from aqueous solution.

2. Material & Methods

All the chemicals and reagents used in present investigation were of extra-pure quality. For preparation of alginate-bentonite clay-activated carbon (ABC) composites, firstly 2% (w/v) sodium alginate solution was prepared by mixing 2 g of sodium alginate (A) in 100 mL deionized water with stirring for 1h, and then 2g of bentonite clay (B) and 2g of Activated carbon (C) were added in individual solution to make different composite and mixture of composites. The mixture was stirred overnight. When the mixture became homogeneous, it was dropped through a burette into 4% (w/v) calcium chloride to form beads with vigorous stirring. The excess unbounded calcium chloride from the bead surface was removed by washing many times with deionized water. The washed beads were then dried for 48 h at room temperature and stored in a clean bottle. The same method was employed for the preparation of A, AB and AC composites. Further, the stock solution of 100 ppm Malachite green was prepared by For experiments the desired concentrations (20, 40 and 80 ppm) of dye solution was prepared by diluting the stock solution using deionizing water.

2.1 Characterization of adsorbents:

Field Emission Scanning Electron Microscope (ZEISS Merlin Compact) at Central Instrumentation Lab Central University of Punjab Bathinda, Punjab, analysed surface morphology of the prepared beads. Further, FTIR spectra of alginate beads before and after adsorption were recorded using FTIR (Bruker, Tensor 27) at Central Instrumentation Lab Central University of Punjab Bathinda, Punjab. The FTIR spectra were taken in the range of 600-4000μm^{-1} as KBr pellet in Attenuated Total Reflectance (ATR) mode. Finally, to confirm the dye adsorption beads were also characterized by Fluorescent micrographs. Weight, size and shape were measured and observe for alginate composite beads.

2.2 Batch adsorption experimental setup:

Batch adsorption experiments were carried out to study the effect of variation in dose, contact time and initial ion concentration on dye adsorption efficiency of alginate beads (A0) and prepared composite materials of alginate [i.e. Alginate-bentonite (AB), activated carbon-alginate beads (AC), and activated carbon-bentonite-alginate beads (ABC)]. In order to study the effect of adsorbent dose on dye adsorption, varying adsorbent dosage (0.5, 1.0 and 1.5 g/L) of all the adsorbent beads under investigation were added to different flasks having 100 mL of 20 ppm

MG dye solution and the flasks were shaken for 2 hrs at room temperature on mechanical shaker (Thermo Scientific MAXQ 6000) at 150 rpm for shaking condition and then left undisturbed for 22 hrs to attain equilibrium. After equilibrium period, the aqueous phase concentration of MG dye was determined by taking absorbance reading at 620 nm using UV- spectrophotometer (Systronics 2201). Further, the effect of variation in contact time and adsorption kinetics of MG adsorption was studied by shaking 0.5g/L dose of adsorbents with 100mL of 20 ppm MG dye solution maintained at neutral pH and the samples were withdrawn at definite time intervals (30, 60, 120 and 240 minutes). Finally, the effect of variation in initial concentration of dye in aqueous solution was studied by shaking 0.5g/L of adsorbents under investigation with 100mL MG solution of varying concentration (20, 40, 60, 80 mg/L) at pH 7. Further, equilibrium study was carried out by applying Langmuir and Freundlich adsorption isotherm models to the data obtained from the experiment to study the effect of initial ion concentration on dye removal.

3. Result and Discussion

3.1 Preparation of Alginate composite:

Total four types of composites were prepared i.e., Alginate beads (A0), Alginate-Activated Carbon (AC), Alginate-Bentonite clay (AB), and Alginate-Activated Carbon-Bentonite clay (ABC). Alginate beads were translucent brownish yellow in color and spherical in shape after drying surface became rougher (Fig.1a). Alginate-Bentonite clay composite beads were dirty yellow-brown in color and opaque in color with the same rough surface after drying (Fig. 1b). Alginate-Activated carbon composite (Fig. 1c) and Alginate- Activated carbon-Bentonite clay beads (Fig. 1d) were black in color due to carbon mixture in the alginate composites.

a. Alginate beads as control beads

b. A-B beads as composite

c. AC beads as composite

d. ABC mix beads as composite

Fig 1. a. Alginate beads as control beads; b. A-B beads as composite; c. AC beads as composite; d. ABC mix beads as composite

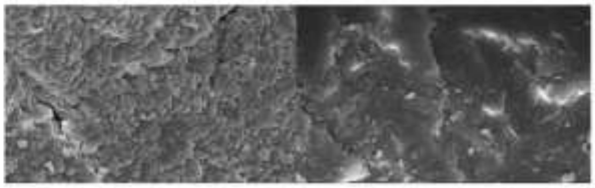
3.2 Physical Characterization of alginate composite beads:

3.2.1 Scanning Electron Microscopy (SEM) analysis:

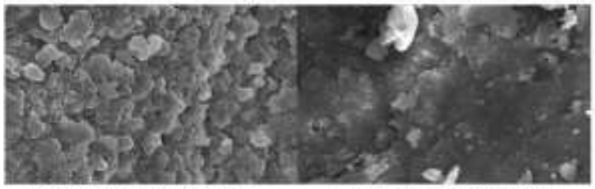
Electron micrographs of the sorbents before and after MG (Malachite green) adsorption are presented in Fig 2 (a-h). The SEM micrographs of the unloaded beads show irregular particles with a rough surface, however, the surface of the adsorbent become smoother due to surface covering with dye molecules after MG adsorption.

3.2.3 FTIR analysis:

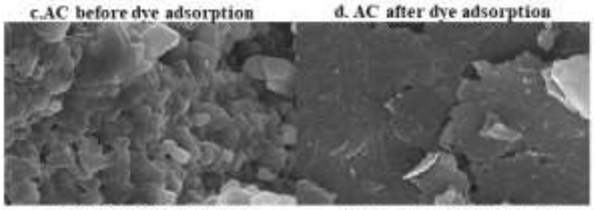
Fourier Transform infrared (FTIR) spectra of A0, AC, AB and ABC after loading of dye are shown in (Fig 3). In all the spectra the broad bands appearing in the range of 3000–3600 cm^{-1} can be attributed to stretching vibrations of OH bonds of sodium alginate. It shows a broad peak at 3416 cm^{-1} in the spectrum of alginate and is attributed to the OH groups, and little change was observed in OH peak intensity after modification of alginate with bentonite and/or activated carbon. The asymmetric and symmetric aliphatic CH stretching bands were observed at 2922 and 2855 cm^{-1}, respectively. The bands at 1628–1631 cm^{-1} and 1431–1458 cm^{-1} observed in the spectra are attributed to the asymmetric and symmetric stretching band vibrations of carboxylate groups (C–O–O) of alginate molecule respectively. As it can be seen from the spectra, the asymmetric and symmetric bands in dye loaded Alginate composites shifts to lower wave numbers compared to the un-adsorbed Alginate composites which could be assigned to the electrostatic binding of MG+ molecules to adsorption sites. The stretching band assigned to the vibration of Si–O was observed at 1031 cm^{-1}. The adsorption process may be physicochemical in nature since there were no suggestive changes in the desorbed Alginate spectra compared to un-adsorbed Alginate spectra (fresh adsorbent). However, all of the adsorption peaks confirm the coating of sodium alginate onto the surface of various composites explained the shift in the IR band of COO^{-} while Alginate interacted with Bentonite clay [16], [17], [18].



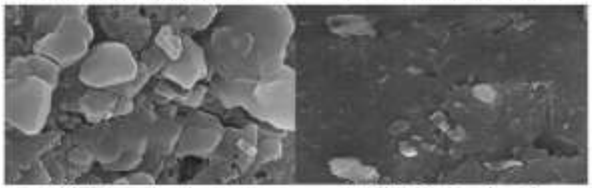
a. Alginate before dye adsorption b. Alginate after dye adsorption



c.AC before dye adsorption d. AC after dye adsorption



e. AB before dye adsorption f. AB after dye adsorption



g. ABC before dye adsorption h. ABC after dye adsorption

Fig 2. Electron micrographs before and after adsorption

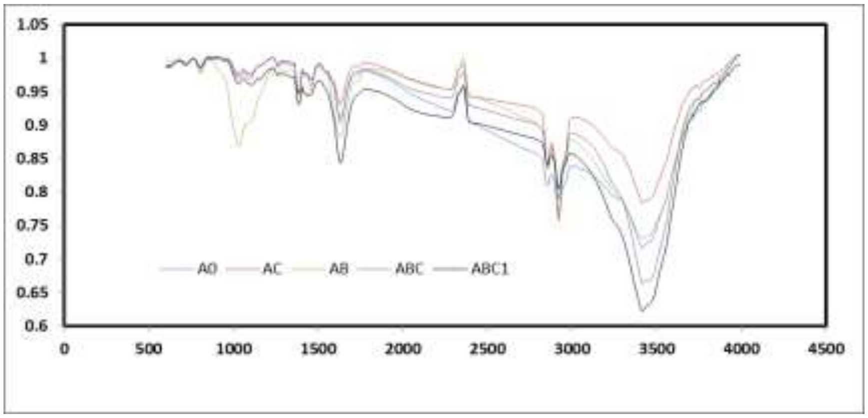
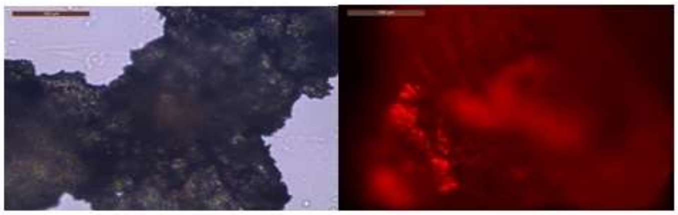


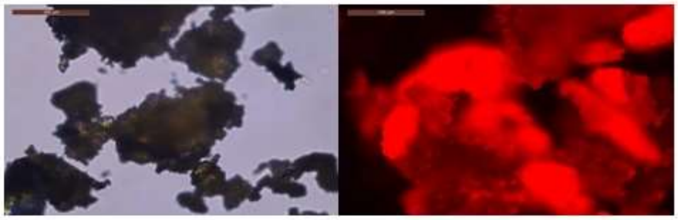
Fig 3. FTIR Spectra of different composites

3.2.4 Fluorescent Microscopy imaging:

As shown in Fig 4, optical microscopic studies were carried out for all alginate composites. They were studied against bright field microscopy and captured using green filter. The images of dye adsorbed beads and alginate composites showed red coloured particles.

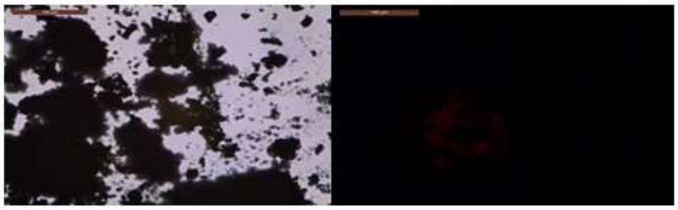


Alginate before dye adsorption **Alginate after dye adsorption**



AB before dye adsorption **AB after dye adsorption**

AC before dye adsorption **AC after dye adsorption**



ABC before dye adsorption **ABC after dye adsorption**

Fig 4. Fluorescence Images before and after adsorption

3.3 Adsorption of Malachite Green on Alginate composites:

3.3.1 Effect of different dosage of Alginate composites:

Effect of adsorbent dosage on MG dye adsorption by all the four adsorbents was investigated by changing the adsorbent dose from 0.5 g/L to 1.5 g/L for 20 mg/L MG dye solution at pH 7. Results indicated that with the increase in adsorbent dose from 0.5 g/L to 1.5 g/L, the percent dye removal increased from 84.40% to 86.95%, 85.20% to 91.80%, 91.50% to 95.30% and 85.80% to 95% in case of A0, AC, AB and ABC, respectively (Fig.5). This can be accredited to the increased number of available adsorption sites due to the increased adsorbent dose which resulted in significant removal of dye from the solution.

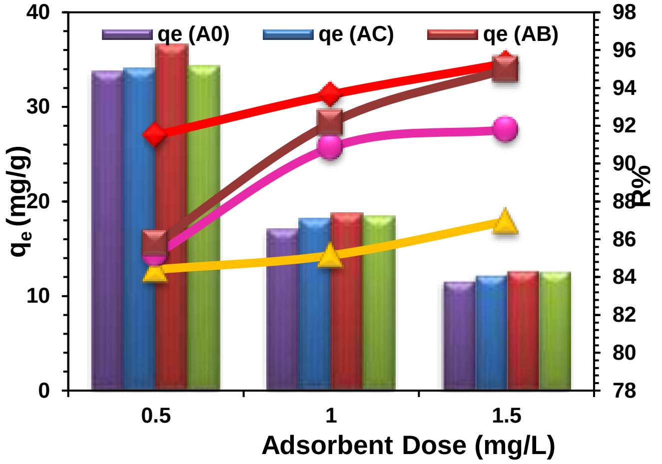


Fig.5. Effect of Adsorption dose on % dye removal and its uptake

3.3.2 Effect of contact time and adsorption kinetic behaviour

From the results it is evident that the rate of dye adsorption was fast at initial stages and then became slower till the attainment of equilibrium. As the contact time increased from 30 to 240 minutes, % dye removal increased from 30.50 to 82.40%, 32.10 to 83.20%, 52.25% to 90% and 32.50% to 84.30% in case of A0, AC, AB and ABC, respectively (Fig. 6). This may be accredited to the fact that at the initial stages more free sites were available near the adsorbent surface due to which there was less hindrance for the approaching dye molecules**. [19], [20]**

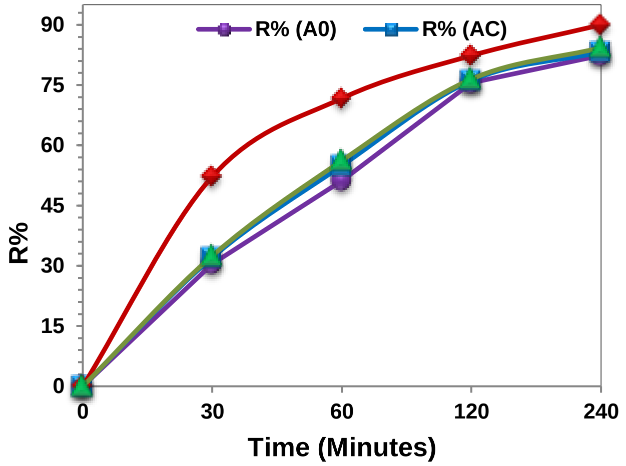


Fig 6: Effect of initial ion concentration on % dye removal

Further, to the data obtained from the above experiment Lagergren pseudo-first-order and pseudo-second-order adsorption kinetic models were applied and it was revealed that dye adsorption on alginate beads A0, AC, AB and ABC beads as composite followed pseudo-second order kinetic model. Fig. 7 represents the linear fit plots of Lagergren pseudo-second order adsorption kinetic plot for A0, AC, AB and ABC with high correlation coefficient. Moreover, for all these adsorbents under investigation, the value of q_e drawn for the same model is in agreement with experimental q_e. The value of pseudo-second-order reaction rate constant (k_2, ads) drawn from the plot for A0, AC, AB and ABC is 0.0006, 0.042, 0.001, 0.0007 min^{-1}, respectively.

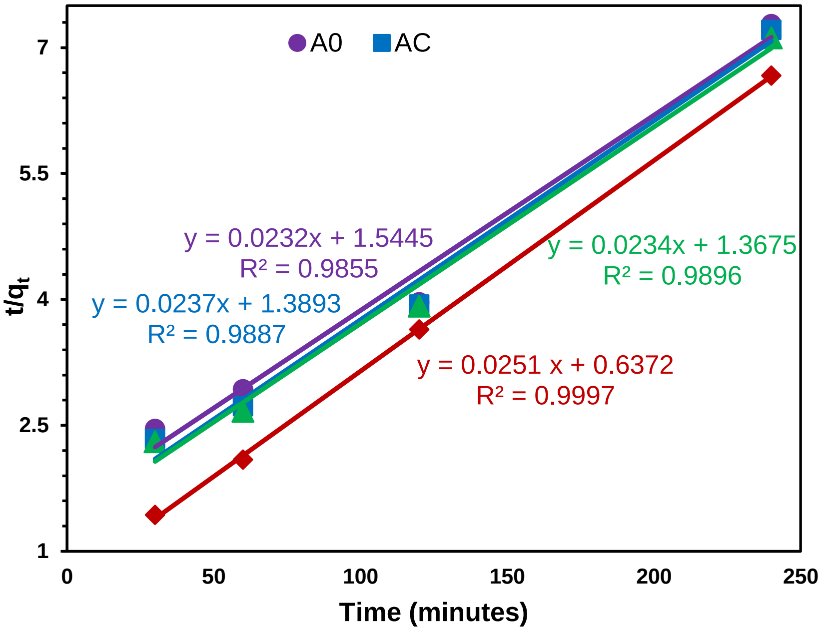


Fig 7: Lagergren Pseudo-second order Adsorption kinetic plot for MG dye Adsorption on A0, AC, AB and ABC

3.3.3 Effect of Initial ion Concentration and Equilibrium studies

It is clearly evident from Fig. 8 that upon increasing the initial concentration of dye in aqueous solution from 20 to 80 mg/L, MG dye uptake increased from 33.76 to 54.24 mg/L for A0, 34.08 to 59.96 mg/L for AC, 36.60 to 69.90 mg/L for AB and 34.32 to 61.54 mg/L for ABC. On the other hand, percentage removal decreased from 84.40 to 33.90%, 85.20% to 37.48%, 91.50% to 43.13% and 85.80% to 38.46% in case of A0, AC, AB and ABC, respectively (Fig. 8) upon increasing the initial concentration of MG dye, which is due to the increased number of dye molecules for the same amount of adsorbent **[20]**

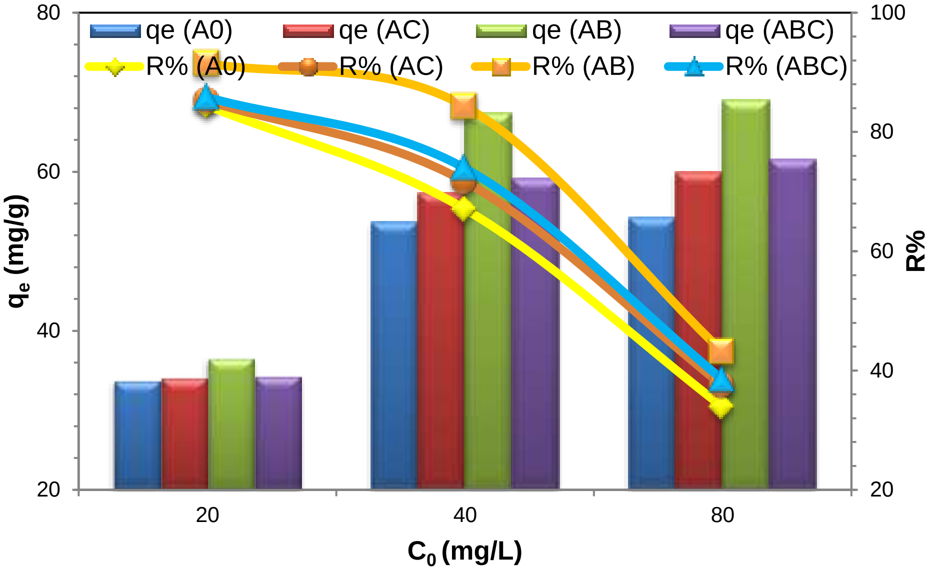


Fig. 8: Effect of initial ion concentration on % dye removal and its uptake

The equilibrium adsorption data was fitted to Langmuir and Freundlich adsorption isotherm models. However, the high correlation coefficient value (R^2) in case of Langmuir adsorption isotherm model for all the adsorbents Fig. 9 and low correlation coefficient value (R^2) in case of Freundlich adsorption isotherm models Fig. 10 indicated that equilibrium adsorption data fits well to Langmuir adsorption isotherm model only which confirms the monolayer adsorption behaviour of dye molecules onto the surface of all the adsorbents under study. Further, values of q_m, adsorption energy (b) and dimensionless factor (R_L) derived from the linear fit diagram of Langmuir adsorption isotherm model are presented in Table 1 below.

It is evident from table 1 that all the values of R_L lies between 0 and 1 in all the cases, which indicates that adsorption of dye molecules on all these adsorbents is favourable[21]

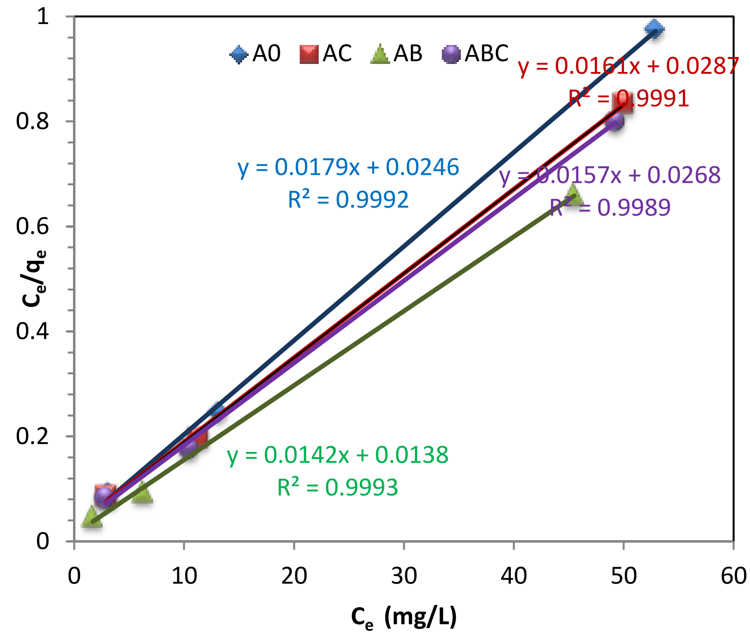


Fig 9: Langmuir isotherm for MG dye adsorption on A0, AC, AB and ABC

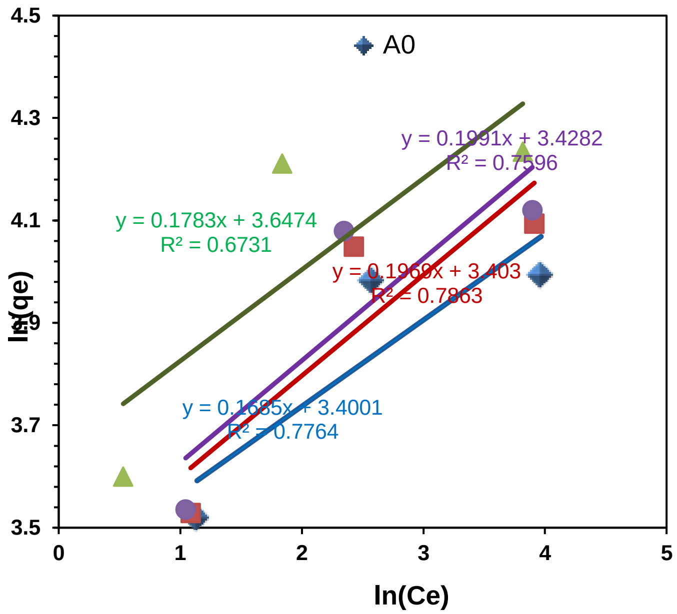


Fig. 10: Freundlich isotherm for MG dye adsorption on A0, AC, AB and ABC

Conclusion

In the present work, alginate beads (A0) and composite materials of alginate [i.e., Alginate-bentonite (AB), activated carbon-alginate beads (AC), and activated carbon-bentonite-alginate beads (ABC)] were prepared and a comparative study on their dye uptake efficiency was carried out. FTIR, SEM and fluorescence microscopic imaging supports adsorption of MG dye. Among the A0, AC, AB and ABC, the highest adsorption is achieved with AB (Alginate bentonite clay beads). The MG dye removal on all these adsorbents followed Lagergren pseudo- second order kinetic models. Equilibrium adsorption data obtained for MG dye removal from aqueous solution by all the adsorbents fits well to Langmuir adsorption isotherm model only, which confirms the monolayer adsorption behavior of dye molecules onto the surface of all the adsorbents under study.

Table 1. Langmuir adsorption isotherm model

Parameters	**A0**	**AC**	**AB**	**ABC**
q_m	58.82	62.50	76.92	66.67
R^2	0.999	0.999	0.999	0.998
b	0.708	0.571	0.928	0.576
R_L	0.026-0.312	0.034-0.372	0.023-0.388	0.034-0.379

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