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Eco-Friendly Method to Detoxify Dyes from Textile Effluent Using Bricks Kiln Chamber Fly Ash as Adsorbent

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Abstract

The feasibility of Brick Kiln Chamber Fly Ash (BKCFA) to remove Methylene blue and Congo red dyes from aqueous solutions were investigated through batch mode studies. Experiments were conducted by varying several parameters namely initial concentration of dye, contact time, adsorbent dose and pH of the dye solution. Kinetics studies of the adsorption revealed that removal of dyes follow first order kinetics. The isotherm for the adsorption of dye on to the BKCFA fit the Freundlich and Langmuir isotherms quiet well. The Scanning electron microscopy (SEM), Energy dispersive analysis of X-ray (EDAX) and FT-IR images of BKCFA before and after adsorption confirmed that the uptake of dyes by brick kiln chamber fly ash.

Keyword: Brick Kiln Chamber Fly Ash (BKCFA), Adsorbent, Methylene blue (MB), Congo red (CR), and Energy dispersive analysis of X-ray (EDAX).

INTRODUCTION

Dyes are released into wastewaters from various industrial units, mainly from the dye manufacturing and textiles and other fabric finishing industries [1]. Most dyes are non-biodegradable in nature which are stable to light and oxidation [2-4]. Improper disposal of these dyes would cause harm to flora and fauna in rivers, lake and sea as they can hamper photosynthesis and can pose, human health risk as they are potentially carcinogenic [5-7]. The unwanted dye pollutants have to be removed from waste waters before being discharged into the environment. Trickling filter, activated sludge, chemical coagulation and flocculation, oxidation, ozonation, membrane separation, photo- degradation, and adsorption processes are most conventional wastewater treatment Technologies [8-11]. Though these techniques are most effective, includes high initial cost and operating cost. Some of them are not feasible on large scale. Physical adsorption has received considerable attention as an effective method for removing the dissolved dyes in waste water [12-13]. The colour removal from textile waste water is considered as an important application of the adsorption process using low-cost adsorbents such as fly ash [14], bagasse fly ash [15], almond seed shell [16], and water hyacinth [17] against expensive adsorbent such as activated carbons. The aim of this study was to investigate the adsorption of Methylene blue and Congo red onto brick kiln chamber fly ash as adsorbent which is a low cost adsorbent for the removal of dye.

MATERIALS AND METHOD

Bricks kiln chamber fly ash (BKCFA) is the solid waste formed during the manufacture of Bricks and it was collected from Bricks kiln located at Ananjioor, Sakkudi post-625020, Othakadai Taluk, Madurai District, Tamilnadu. The collected BKCFA was washed with D.D water several times to remove water soluble impurities. Then it was dried by placing in a hot air oven at the temperature of 110°C for three hours. The dried BKCFA was sieved into 90 micron particle size and stored in an air tight bottle. Analytical reagent grade Methylene blue and Congo red dye were used for making stock solution for synthetic textile effluents. The solutions of different initial concentrations were prepared by diluting the stock solution in appropriate proportions. Batch adsorption experiments were carried out to find out the optimum conditions for maximum removal of Methylene blue and Congo red dye using BKCFA as adsorbent. The concentrations of the dye solutions after adsorptions were determined spectrophotometrically (using Elico make Bio-UV spectrophotometer, Model BL-192). The adsorption data obtained in batch studies were used to calculate the percentage of removal of dye and adsorbed dye amount by using the following equation 1 and 2.

$$\text{Percentage removal} = [(C_i - C_o) / C_i] \times 100 \ldots (1)$$

$$\text{Percentage adsorbed} = [(C_i - C_o)\, v / m] \times 100 \ldots (2)$$

Where C_i and C_o are the initial and equilibrium concentration in mgL^{-1} of the dye solution respectively and V is the volume of the solution and in m is the adsorbent mass (g). The adsorbent BKCFA was characterized by FT-IR, SEM and EDAX techniques in order to confirm the existence of micro pores and meso pores which are responsible for the removal of dyes and also confirm the dyes removal efficiency of the adsorbent.

RESULT AND DISCUSSION

Characterization of BKCFA

FT-IR spectrum of the BKCFA before and after adsorption of Methylene blue and Congo red dye were recorded and reproduced in Fig.1, 2 & 3. The shifting and disappearance of stretching vibrations after adsorption supported that the functional groups on the surface of BKCFA are participated Methylene blue and Congo red dye removal process.

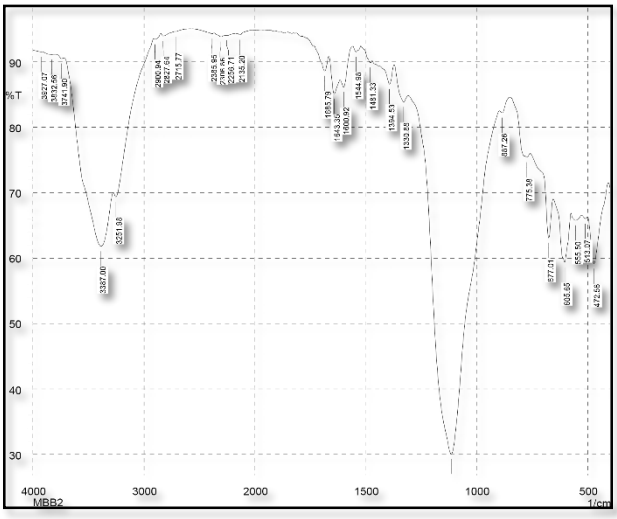

Figure 1. FT- IR spectrum of BKCFA before adsorption

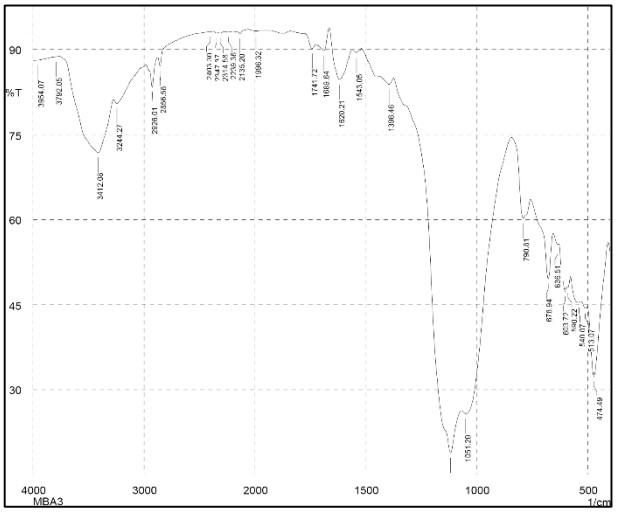

Figure 2. FT-IR spectrum of BKCFA-Methylene blue dye

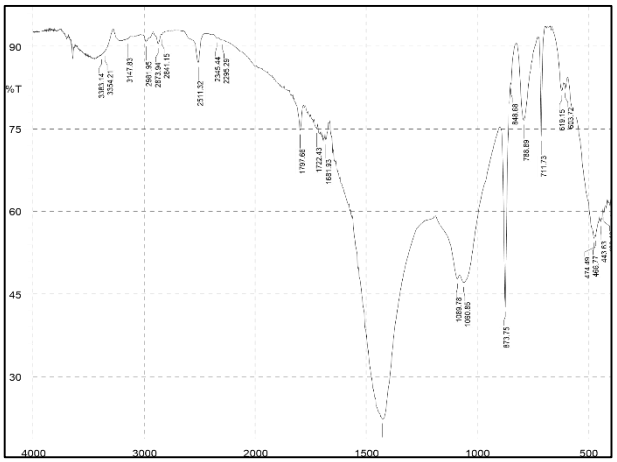

Figure 3. FT-IR spectrum of BKCFA-Congo red dye

SEM image of BKCFA before and after adsorption of Methylene dye and Congo red dye were recorded and reproduced in Fig. 4, 5 & 6.

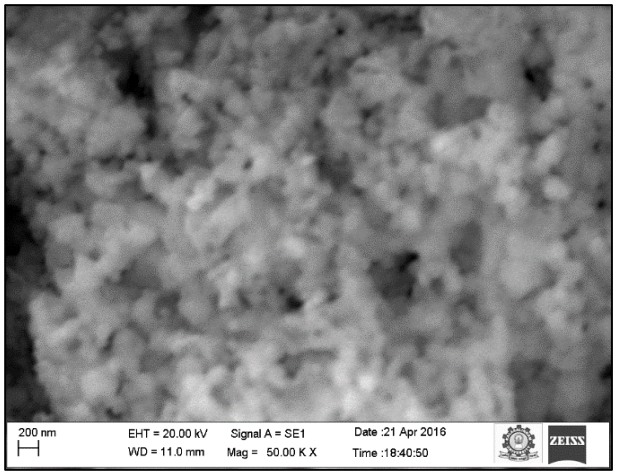

Figure 4. SEM image of BKCFA before adsorption

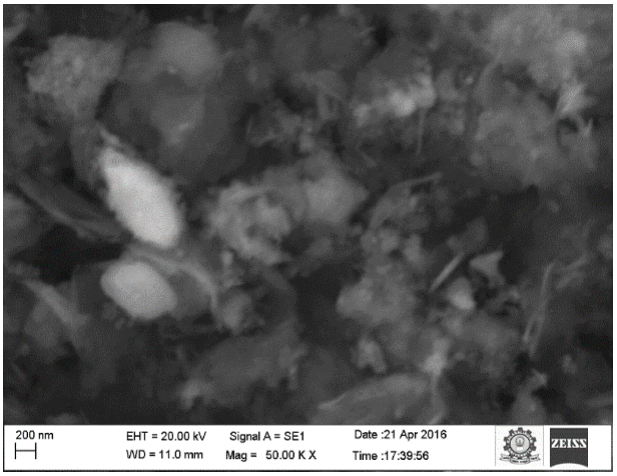

Figure 5. SEM images of BKCFA-Methylene blue dye

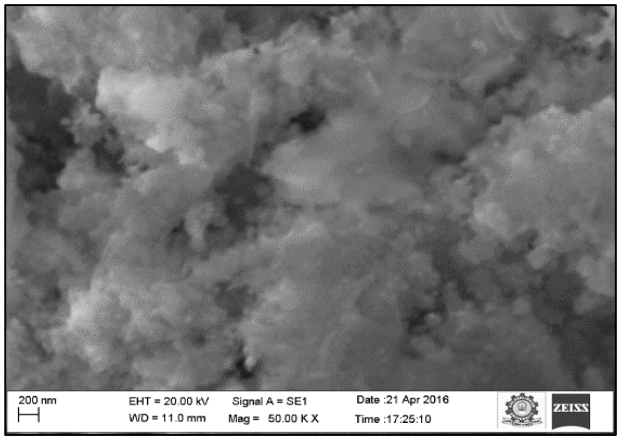

Figure 6. SEM images of BKCFA-Congo red dye

The SEM image of BKCFA before adsorption indicates that the existence of micro and meso pores which are responsible for the removal of dyes from waste water. The fading of pores nature in the SEM image of BKCFA- Methylene blue and BKCFA-Congo red dye supported that the Methylene blue and Congo red dye are incorporated into the pores of the adsorbent. The EDAX spectrum for BKCFA before and after adsorption of Methylene blue and Congo red dyes were recorded and reproduced in Fig.7 – 9. The EDAX spectrum of BKCFA after adsorption of Methylene blue and Congo red with trace nitrogen were also recorded and reproduced in fig. 10,11

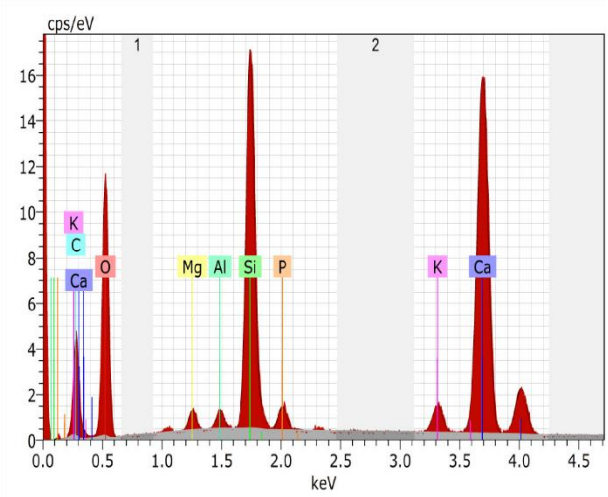

Figure 7. EDAX spectrum of BKCFA before adsorption

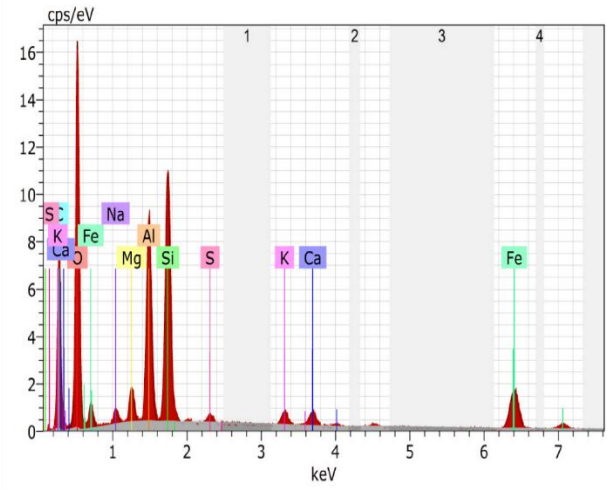

Figure 8. EDAX spectrum of BKCFA-Methylene blue dye

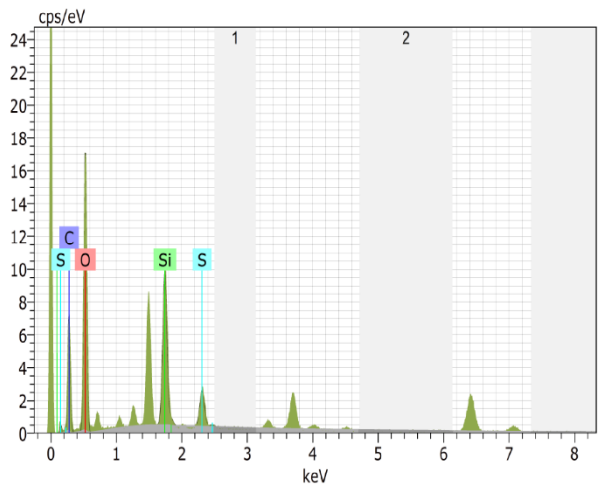

Figure 9. EDAX spectrum of BKCFA-Congo red dye

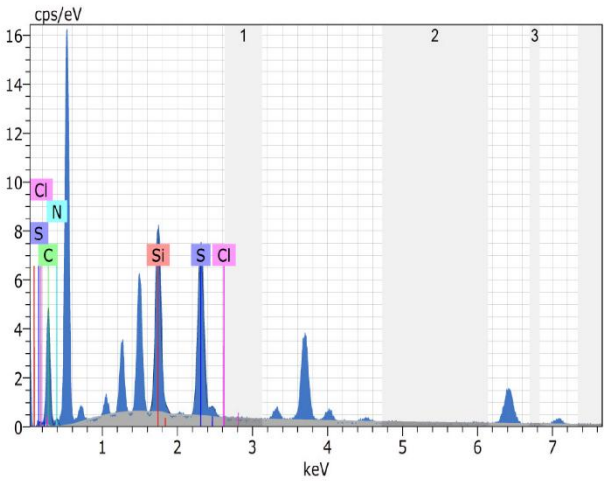

Figure 10. EDAX spectra of BKCFA after adsorption of Methylene blue with trace nitrogen

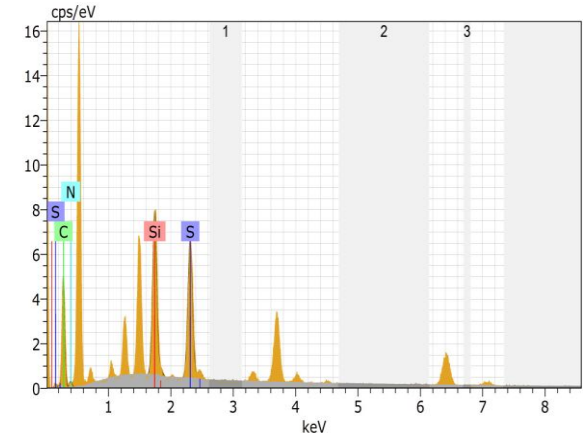

Figure 11. EDAX spectrum of BKCFA-Congo red dye with trace nitrogen

EDAX spectrum of BKCFA indicates that the adsorbent is the oxides form of various metals and contaminated with carbon residue. The appearance of new peaks for nitrogen and sulphur and increase in percentage of carbon and oxygen in EDAX spectrum of BKCFA after adsorption of Methylene blue dye and Congo red dye supported that the adsorption of Methylene blue dye and Congo red dye on BKCFA adsorbent.

Adsorption studies

Initial concentration of the dye solution, dose of the adsorbent, contact time and pH of the dye solution are the important parameter influencing the mechanism of the adsorption and the efficiency of the removal of dyes by adsorption on BKCFA. The optimum conditions for the maximum removal of Methylene blue and Congo red dye were determined on varying any one of the parameters by keeping all other parameters as constant. The effect of initial concentration on the percentage removal of Methylene blue and Congo red dye by adsorption on BKCFA adsorbent is shown in Fig.12.

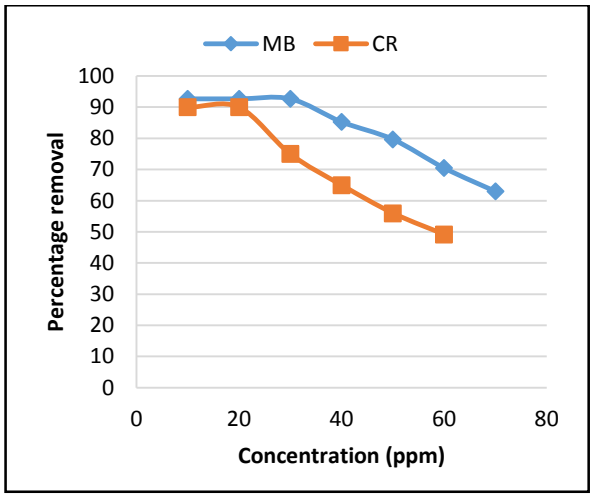

Figure 12. Effect of initial concentration

The percentage removal of dyes found to decrease with increase in initial concentration of the dye solutions. It is due to that, after the formation of mono layer of the respective dye molecules at the surface of BKCFA, the formation of second layer of dye molecules is highly hindered at higher initial concentration, due to the repulsive interaction between adsorbed and unabsorbed dyes present on solid surface and in solution [18], respectively. The optimum concentration for maximum percentage removal of Methylene blue and Congo red dye by adsorption on BKCFA was found to be 30 ppm and 20ppm respectively.

The effect of contact time on the removal of Methylene blue and Congo red dye by adsorption on BKCFA is shown in Fig.13.

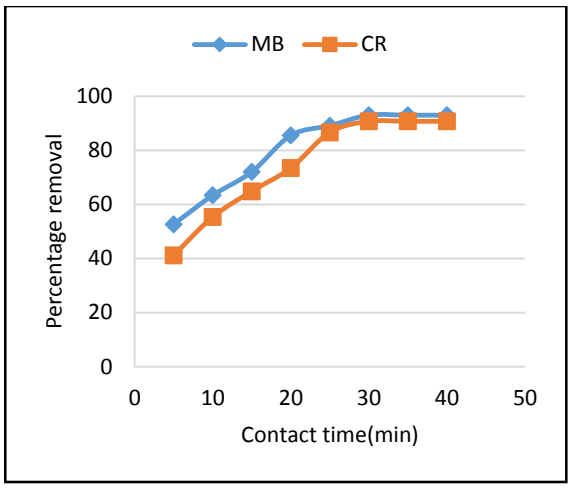

Figure 13. Efffect of contact time

It is observed that the percentage removal of dyes increases as the contact time increases and reaches a maximum value. Similar results have been reported by many researchers [19-21]. The optimum contact time for maximum percentage removal of methylene blue dye and Congo red dye by adsorption on BKCFA was found to be 30 minutes.

The effect of dose rate on the percentage removal of Methylene blue dye and Congo red dye by adsorption on BKCFA is shown in Fig.14.

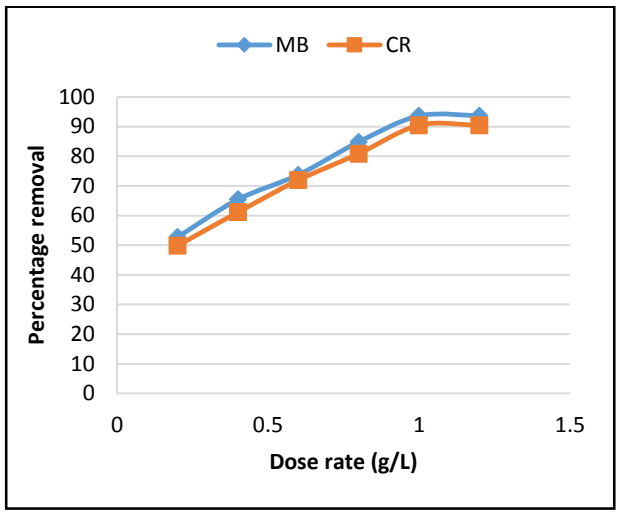

Figure 14. Effect of dose of adsorbent

The percentage removal of dyes increases with increase in adsorbent dose rate. This is due to the increase in number of active sites of adsorbent with increase in dose of the adsorbent [22, 23]. The optimum dose rate for maximum percentage removal of Methylene blue dye and Congo red dye by adsorption on BKCFA was found to be $1gL^{-1}$.

The pH of the dyes solution and the point of zero charge of BKCFA (pH_{pzc}) are the important factors controlling the adsorption of dyes on to BKCFA [24]. The pH_{pzc} of BKCFA was determine as described by the solid addition method using KNO_3(0.01M)[25]. solution and the determined value is 7.9.

At a solution of pH less than 7.9 the surface becomes positively charged and pH greater than 7.9 the BKCFA surface is negatively charged. The effect of pH on the percentage removal of Methylene blue and Congo red dye by adsorption of BKCFA is shown in Fig.15. It was observed that the adsorption efficiency increased from 70.7% to 98.1% as pH increases from 2 to 11 for methylene blue dye and the adsorption efficiency decreases from 98.5% to 70.1 % as pH increases from 4 to 9 for Congo red dye. For methylene blue dye removal, the pH of the system increases and H+ ion concentration decreases, the number of the negatively charged sites increases that enhance the removal of methylene blue dye by facilitating the electrostatic attraction between negatively charged adsorbent and positively charged methylene blue dye[26]. For Congo red dye removal, adsorbent surface is protonated at an acidic pH condition and they favour the adsorption of the anionic Congo red dye due to electrostatic attraction. With an increasing pH of the dye solution, the surface groups are deprotonated resulting in an increase of negatively charged sites that inhibit the adsorption of the anionic dye due to electrostatic repulsion [27-29]. The optimum pH for maximum removal of methylene blue dye and Congo red dye on to BKCFA were found to be 11 and 4.

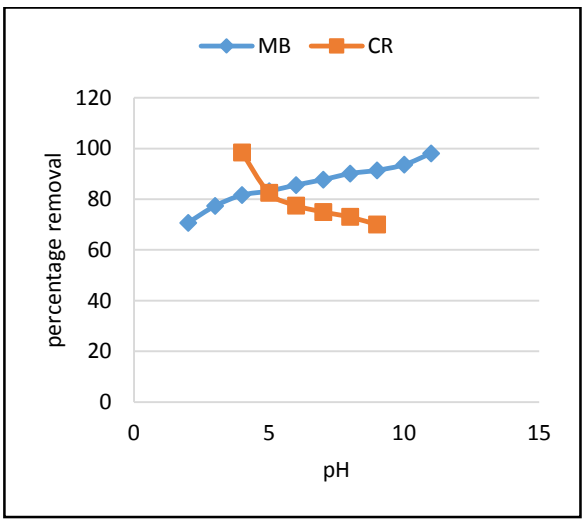

Figure 15. Effect of pH

Adsorption isotherm

The equilibrium data for the removal of Methylene blue and Congo red dyes were modeled with Freundlich [30] and Langmuir [31] isotherm. The Freundlich and Langmuir isotherm plots are shown in Fig.16 and 17.

Freundlich isotherm : $\log (x/m) = \log k + (1/n) \log C_e$

Langmuir isotherm : $(C_e / q_e) = (1/Q_o b) + (C_e / Q_o)$

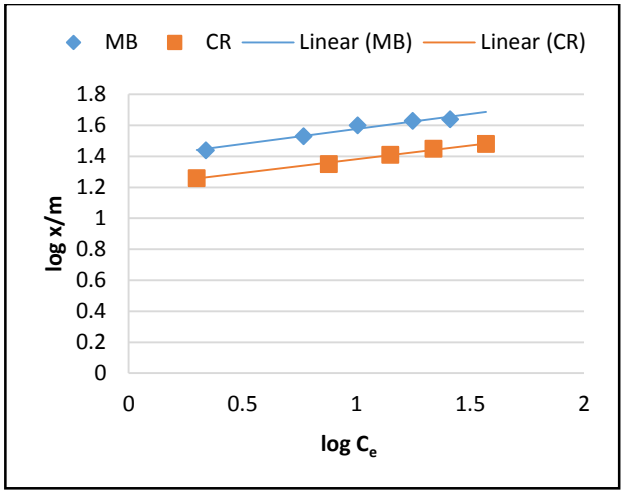

Figure 16. Freundlich isotherm plots

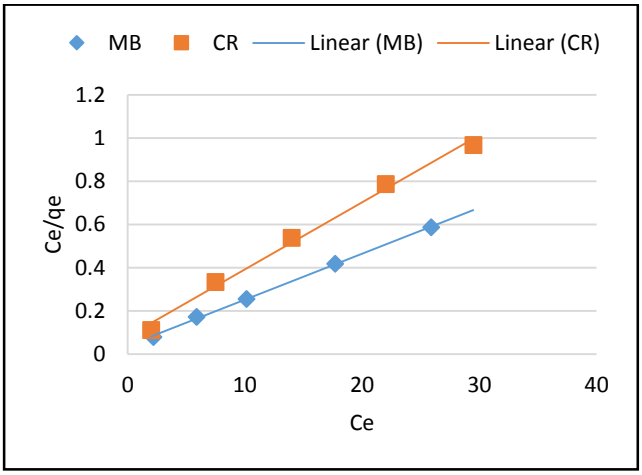

Figure 17. Langmuir isotherm plots

The results indicates that the applicability of these adsorption isotherms for the removal of Methylene blue dye and Congo red dye by BKCFA. The essential parameters like separation factor R and adsorption intensity (1/n) calculated from the above models are listed in Table 1.

Table 1. Values of Freundlich and Langmuir constants

S.No	Parameter	Value	
		CR	MB
I	**Freundlich isotherm**		
	Adsorptionintensity(1/n)	0.178	0.169
	Intercept (logk)	1.20	1.39
	Adsorption capacity(k)	15.85	24.55
II	**Langmuir isotherm**		
	Slope ($1/Q_o$)	0.030	0.021
	Energy(b)	0.366	0.538
	Separation Factor(R)	0.120	0.058
	Adsorption capacity (Q_0)	33.3	47.62

The calculated value of 1/n and R falls in between 0 to 1 indicates that the feasibility of adsorption. The adsorption capacity of BKCFA adsorbent towards Methylene blue dye is greater than Congo red dye.

Kinetics of adsorption

Kinetics of adsorption data were studied by applying the kinetic equations like Natarajan and Khalaf [32] (plot of log C_0/C_t vs time), Lagergren [33], (plot of log (q_e-q_t) vs time, Bhattacharya and Venkobachar [34] (plot of 2+log[1-U(t)] vs time), and intra particle diffusion equation [35] (plot of x/m vs $t^{1/2}$). These plots are given in the fig 18-21.

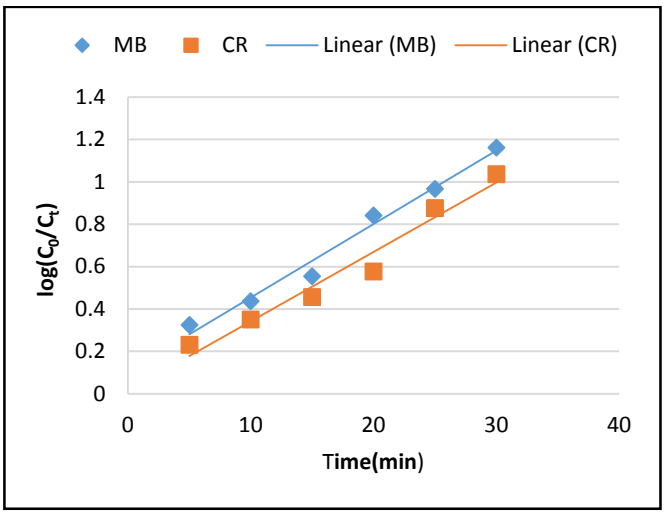

Figure 18. Natarajan and Khalaf plots

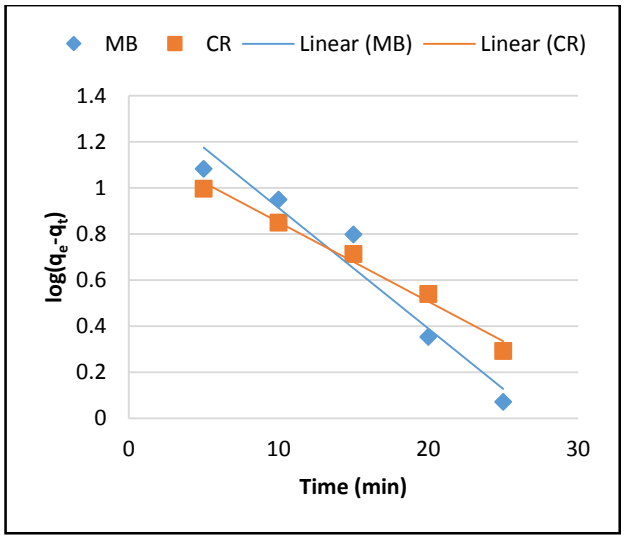

Figure 19. Lagergren plots

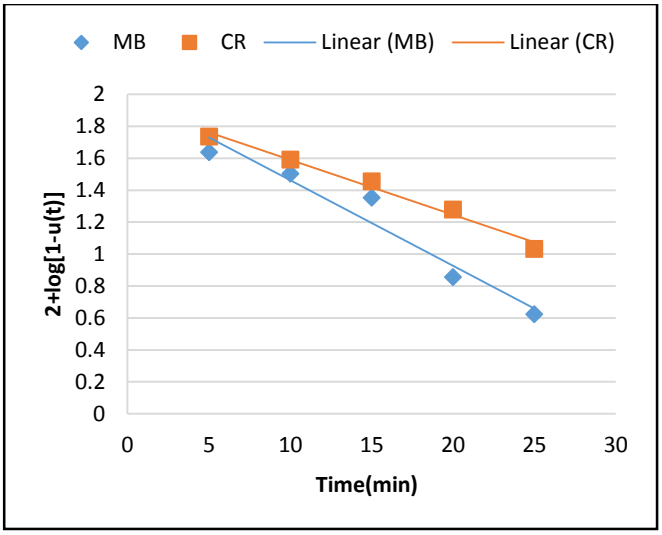

Figure 20. Bhattacharya and Venkobachar plots

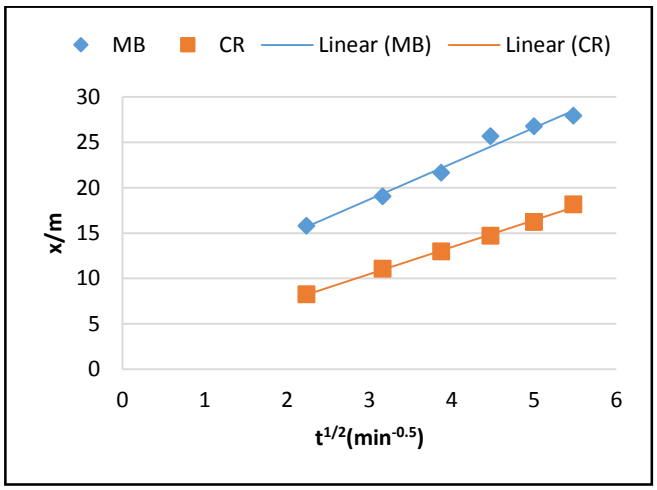

Figure 21. Intra particle diffusion equation plots

The rate constants and intra- particle diffusion co-efficients calculated from the above plots for the removal of Methylene blue dye and Congo red dye by BKCFA are given in table 2.

Table 2. Rate constants for the adsorption of Congo red dye and Methylene blue dye on BKCFA.

S. No	Kinetic equation	Rate constant (10^{-2} min^{-1})	
		CR	MB
1	Natarajan and Khalaf	7.4	8.1
2	Lagergren	7.8	12.1
3	Bhattacharya and Venkobachar	7.9	12.2
4	Intra particle diffusion	Intra particle diffusion coefficient (10^{-2} $min^{-0.5}$)	
		297.6	395.0

The straight line plots for the above equation shows that the adsorption follows first order kinetics. The linearized plot for intra-particle diffusion model equation shows that intra-particle diffusion is the rate determining step. Greater the intra-particle diffusion coefficient greater the rate of adsorption. The rate constant of adsorption is higher in the case of Methylene blue dye than Congo red dye

CONCLUSION

The results of present studies shows that Brick Kiln Chamber Fly Ash (BKCFA) is a metal oxides, micro porous and meso porous material which is used as an effective adsorbent for removing Methylene blue dye and Congo red dye from textile effluents. The adsorption of Methylene blue dye and Congo red dye were strongly dependent on pH, and the maximum removal was attained at pH 11 for Methylene blue dye and at pH 4 for Congo red dye. The optimum concentration for maximum removal of methylene blue dye and Congo red dye by adsorption onto BKCFA were found to be 30 ppm and 20 ppm.The removal efficiency of BKCFA increases with increase in contact time and dose rate. The adsorption data were described well with Freundlich and Langmuir isotherms. Kinetic studies demonstrated that the adsorption mechanism of Methylene blue dye and Congo red dye follows first order kinetics and the Methylene blue dye removed faster than Congo red dye by adsorption on BKCFA. Hence the low cost Brick Kiln Chamber Fly Ash is the best alternate for high cost commercial activated carbon for the removal of dyes from textile effluents.

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