Original Research Paper

Chemistry

ADSORPTION DYNAMICS AND EQUILIBRIUM UPTAKE OF DYES USING BRICK KILN ASH

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ABSTRACT The feasibility of brick kiln ash (BKA) to remove Congo red and Malachite green 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 BKA fit the Langmuir isotherm quilt well. The Scanning electron microscopy(SEM), Energy dispersive analysis of X-ray(EDAX) and FT-IR images of BKA before and after adsorption confirmed that the uptake of dyes by brick kiln fly ash.

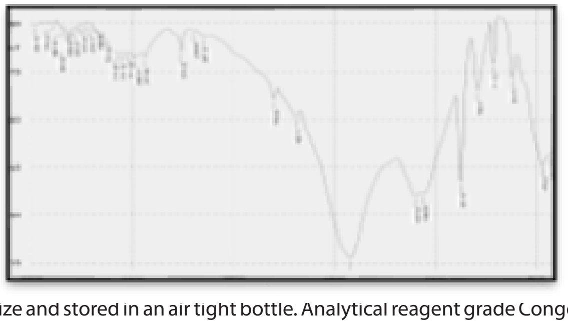
KEYWORDS : Brick Kiln Ash (BKA), Adsorbent, Congo red (CR), Malachite Green (MG) dyes and EDAX.

1. INTRODUCTION

Dyes are released into wastewaters from various industrial units, mainly from the dye manufacturing and textiles and other fabric finishing industries1. Most dyes are non-biodegradable in nature which are stable to light and oxidation2-4. 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 carcinogenic5-7. The unwanted dye pollutions 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 concentration of dissolved dyes in waste water12,13. The colour removal from textile waste water is considered as an important application of the adsorption process using low-cost adsorbents such as fly ash14, bagasse fly ash15, almond seed shell16, water hyacinth17 against expensive adsorbents such as activated carbon. The aim of this study was to investigate the adsorption of Congo red and Malachite green dyes onto brick kiln ash as adsorbent which is a low cost adsorbent for the removal of dye.

2. MATERIALS AND METHOD

Bricks kiln ash (BKA) is the solid waste formed during the manufacture of Bricks and it was collected from Bricks kiln located at Valliyoor in Trinelveli district, Tamilnadu. The collected BKA 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 BKA was sieved into 90 micron particle

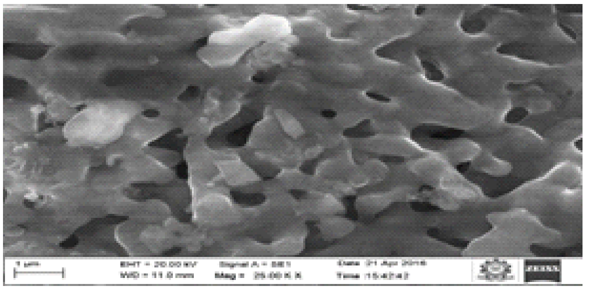


size and stored in an air tight bottle. Analytical reagent grade Congo red dye and Malachite green dye were used for making stock solution for synthetic textile effluents. The solutions of different initial concentrations were prepared by diluting the stock solution in appropriate proportions. Batch adsorption experiments were carried out to find out the optimum conditions for maximum removal of Congo red and Malachite green dyes using BKA 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.

Percentage removal = $[(C_i – Co) / C_i] \times 100$… (1)

Percentage adsorbed = $[(C_i – C_o) v / m] \times 100$… (2)

Where Ci and Co are the initial and equilibrium concentration in mgL-1 of the dye solutions respectively and V is the volume of the solution and in m is the adsorbent mass (g).



3. RESULT AND DISCUSSION

3.1 Characterization of BKA

FT-IR spectrum of the BKA before and after adsorption of Congo red and Malachite green dyes 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 BKA are participated in Congo red and Malachite green dyes removal process.

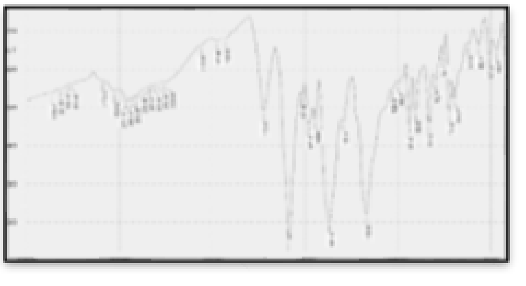


Fig.1 FT- IR spectrum of BKA before adsorption
Fig.2 FT-IR spectrum of BKA-Congo red dye

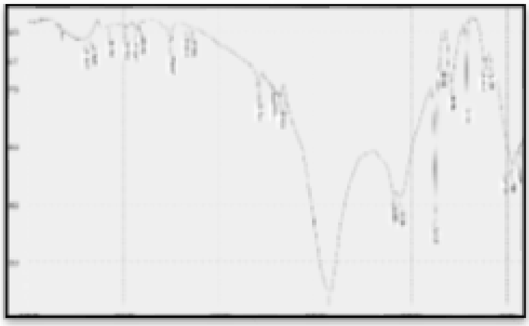
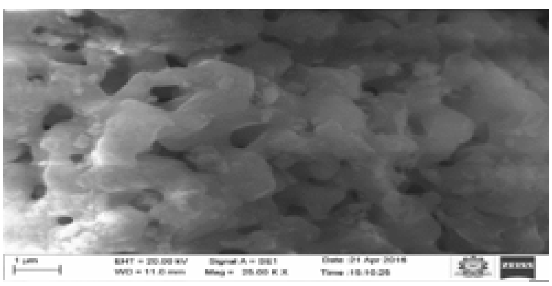


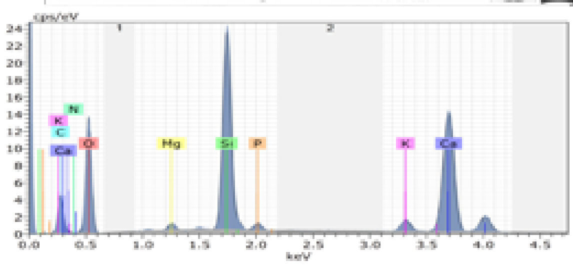
Fig.3 FT-IR spectrum of BKA-Malachite green dye

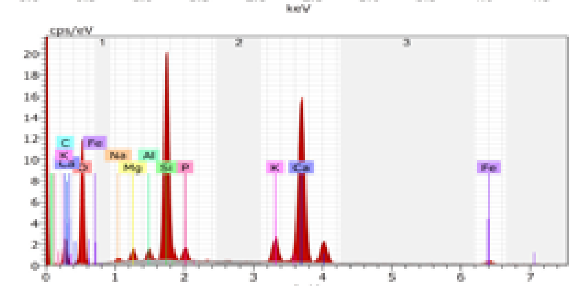
SEM image of BKA before and after adsorption of Congo red dye and Malachite green dye were recorded and reproduced in Fig. 4, 5 & 6.

Fig.4 SEM image of BKA before adsorption
Fig.5 SEM images of BKA-Congo red dye
Fig.6 SEM images of BKA-Malachite green dye

The SEM image of BKA 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







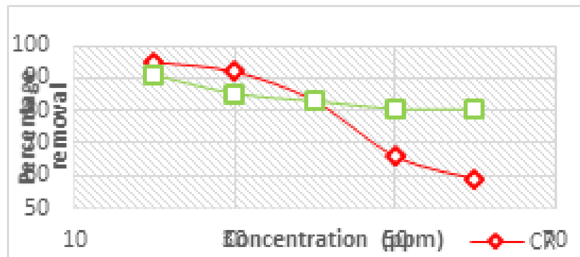
nature in the SEM image of BKA- Congo red and BKA-Malachite green dye supported that the Congo red and Malachite green dye are incorporated into the pores of the adsorbent. The EDAX spectrum for BKA before and after adsorption of Congo red and Malachite green dyes were recorded and reproduced in Fig.7, 8 & 9.

Fig.7 EDAX spectrum of BKA before adsorption
Fig.8 EDAX spectrum of BKA-Congo red dye
Fig.9 EDAX spectrum of BKA-Malachite green dye

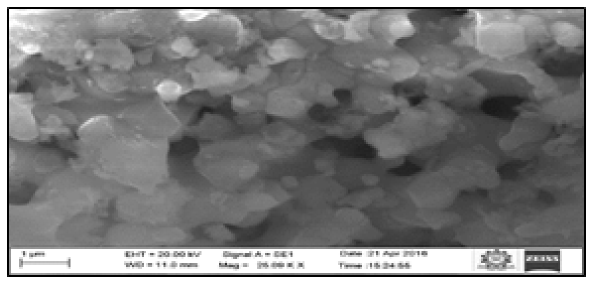
EDAX spectrum of BKA indicates that the adsorbent is the oxides form of various metals and contaminated with carbon residue. The appearance of new peaks for nitrogen and sulphur and increase in percentage of carbon and oxygen in EDAX spectrum of BKA-Congo red dye supported that the adsorption of Congo red dye on BKA adsorbent. The apperance of new peak for nitrogen and increase in percentage of carbon and oxygen in the EDAX spectrum of BKA-Malachite green dye supported that the adsorption of malachite green dye on BKA adsorbent.

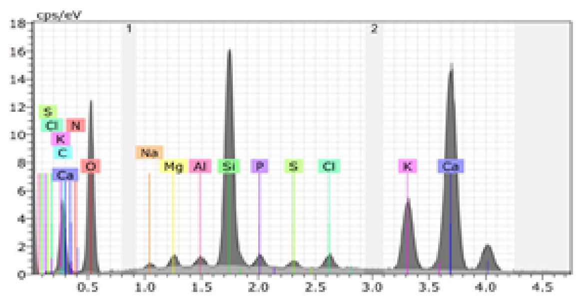
3.2 Adsorption studies

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 BKA. The optimum conditions for the maximum removal of Congo red dye and Malachite green dye were determined on varying all parameters by keeping any one of the parameter as constant. The effect of initial





concentration on the percentage removal of Congo red dye and Malachite green dye by adsorption on BKA adsorbent is shown in Fig.10.

Fig.10.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 BKA, 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 solution18, respectively. The optimum concentration for maximum percentage removal of Congo red dye and Malachite green dye by adsorption on BKA was found to be 20ppm. The effect of contact time on the removal of Congo red dye and Malachite green dye by adsorption on BKA is shown in Fig.11.

VOLUME-6, ISSUE-7, JULY-2017 • ISSN No 2277 - 8160

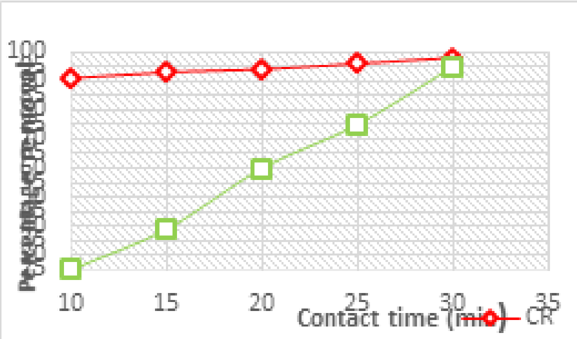


Fig.11 Efffect of contact time

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 Congo red and Malachite green dyes by adsorption on BKA was found to be 30 minutes.

The effect of dose rate on the percentage removal of Congo red and Malachite green dyes by adsorption on BKA is shown in Fig.12.

Fig.12 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 Congo red dye and Malachite green dye by adsorption on BKA was found to be 10gL-1 and 5gL-1. The effect of pH on the percentage removal of Congo red dye and Malachite green dye by adsorption of BKA is shown in Fig.13.

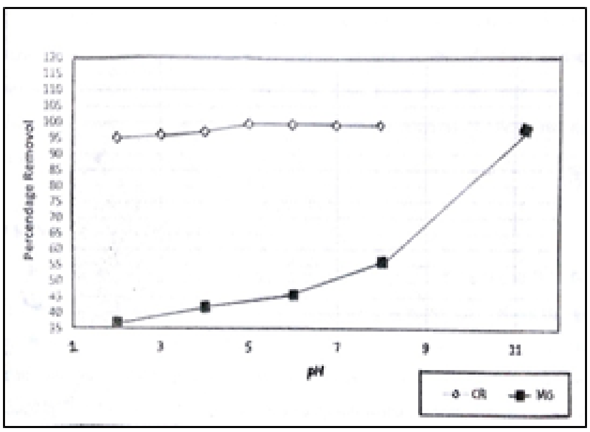
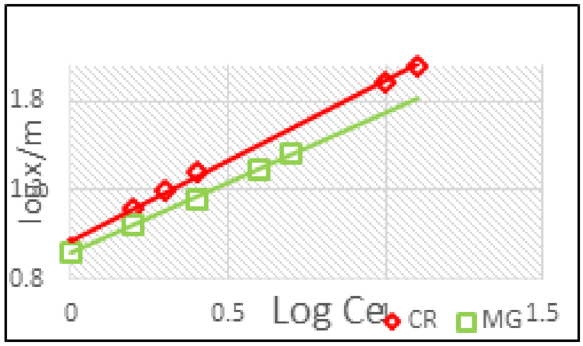


Fig.13 Effect of pH

For Malachite green dye the maximum removal occurs at pH: 11.6. The adsorption of positively charged dye on the adsorbent surface is primarily influenced by the surface on the adsorbent which in turn is influenced by the solution pH. The result showed that availability of negatively charged groups at the adsorbent surface which is necessary for the adsorption of basic dyes. There is a net positive charge in the adsorption system due to the presence of H3+O at pH 2. Thus, as the pH increases, more negatively charged surface was available which facilitating the greater removal of Malachite green dye at higher pH level. For Congo red dye the maximum removal occurs at pH 4-5. This results showed that availability of positive charged groups at the adsorbent surface responsible for the adsorption of acidic dye. Thus lower pH level, more positively charged surface was available on facilitating greater removal of Congo red dye at lower pH level.

3.3 Adsorption isotherm

The equilibrium data for the removal of Congo red dye and Malachite green dye were modeled with Freundlich24 and Langmuir25 isotherm. The Freundlich and Langmuir isotherm plots are shown in Fig.14 and 15.



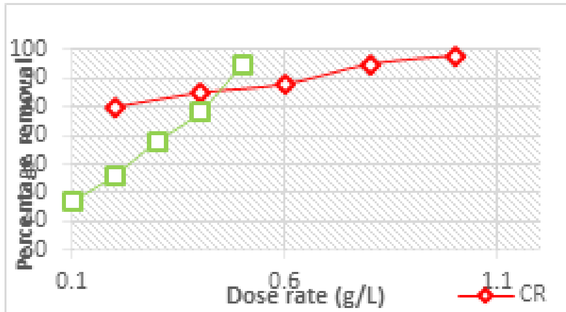


Fig.14 Freundlich isotherm plots

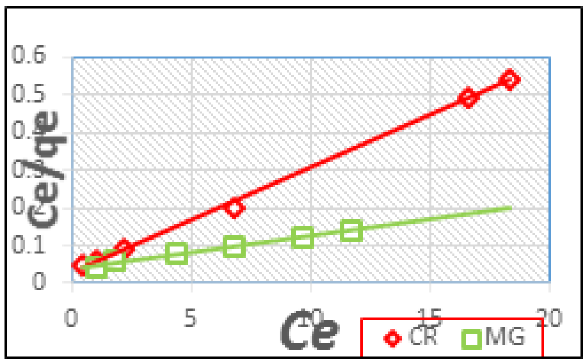


Fig.15 Langmuir isotherm plots

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	Kinetic equation	Rate constant (10-2 min-1)	
		CR	MG
1	Natarajan and Khalaf	3.6	6.5
2	Lagergren	0.999	1.4

S.No.	Parameter	Value	
		CR	MG
1.	Freundlich isotherm Slope(1/n) Intercept (logk) Adsorption capacity (k)	0.2857 1.2800 19.05	0.6363 1.57 37.15
2.	Langmuir isotherm Slope (1/Qo) b RL Q0	0.0197 1.0003 0.0476 50.76	0.0078 1.000 0.0476 128.20

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

3.4 Kinetics of adsorption
Kinetics of adsorption were studied by Natarajan and Khalaf26 and Lagergren27 first order kinetics equations. A linear relationship was found out with each equation and the plots are given in Fig 16 & 17.

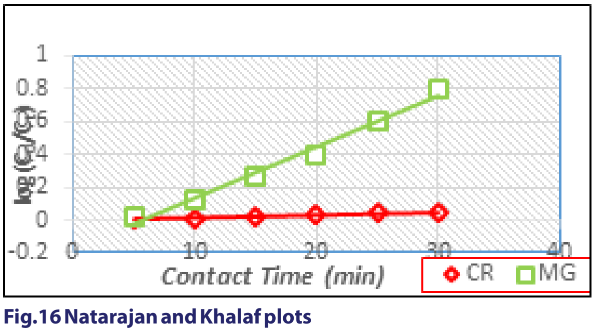


Fig.16 Natarajan and Khalaf plots

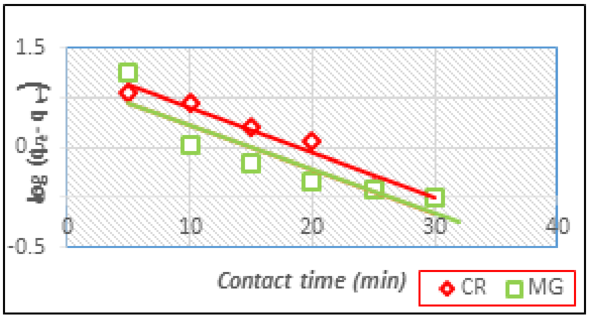


Fig.17 Lagergren plots

The rate constants calculated from the above equations are given in table 2.

The rate constant of adsorption is higher in the case of Malachite green dye than Congo red dye.

4. CONCLUSION
The results of present studies shows that Brick Kiln Ash (BKA) is a metal oxides, micro porous and meso porous material which is used as an effective adsorbent for removing Congo red dye and Malachite green dye from textile effluents. The adsorption of Congo red dye and Malachite green dye were strongly dependent on pH, and the maximum removal was attained at pH 4-5 for Congo red dye and at 11.6 for Malachite green dye. The removal efficiency of BKA increases with increase in contact time and dose rate. The adsorption data was described well with Freundlich and Langmuir isotherms. Kinetic studies demonstrated that the adsorption mechanism of Congo red dye and Malachite green dye follows first order kinetics and the Malachite green dye removed very faster than Congo red dye by adsorption on BKA. Hence the low cost Brick Kiln Ash is the best alternate for high cost commercial activated carbon for the removal of dyes from textile effluents.

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