Adsorptive Removal of Brilliant Green Dye from Wastewater by Zeolite Synthesized from Coal Fly Ash

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***Abstract*:** Adsorption of Brilliant Green dye using zeolite was synthesized from coal fly ash by direct hydrothermal treatment with sodium hydroxide at different concentration ratios at temperature 550 °C and activation time of 4 hrs. The adsorbent was characterized by XRF, SEM, XRD and FTIR. It was used as low cost adsorbent for the removal of brilliant green dye from wastewater. Batch studies were carried out to study the effect of contact time, pH, adsorbent doses, adsorbate concentration and temperature. The results of batch studies revealed that the adsorption of brilliant green was strongly pH dependent and maximum brilliant green removal was observed at equilibrium pH of 5.0. Optimum adsorbent dose and contact time were found to be 15 g/l and 120 minutes respectively. Kinetic studies have been performed to have an idea of the mechanistic aspects of the process. The result also shows that adsorption increases with increase in temperature thereby showing the process endothermic in nature. Adsorption data have been correlated with Langmuir and Freundlich isotherm models.

Key words: Brilliant Green, Fly ash, Zeolite, Adsorption.

I. INTRODUCTION

Environmental pollution is a major problem throughout the world. Development of industries has led to the problem of different types of pollution. Because of scarcity of water in many areas we are in need to preserve the available water. Earlier it was believed that the water bodies like oceans were very large to pollute (Aksu, 2005).

Dyes are used in almost every industry from textile to food industries to color their products. Disposal of dyeing industry wastewater pose one of the major problem. Most of the synthetic dyes used for colorization in different industries like dyestuffs, textile, leather, paper and plastic use dye in order to color their products and also consume substantial volume of water. As a result they generate a considerable amount of colored water. Thus, the disposal of dyes and pigments into aqueous environment is a main serious environmental problem (Ghouti et al, 2003, Allen et al, 2003, Armagan et al , 2003, Armagan et al, 2006).

Many types of wastes from industries are produced by various processes in industries which releases materials that are noted as useless while manufacturing a product. Industrial wastes are in various forms like toxic waste, chemical waste, industrial solid waste and municipal solid waste.

Disease spreads by consumption of polluted water. It has been estimated that 50,000 people die daily world-wide as a result of water-related diseases (Banat et al, 1996). It also contains viruses, bacteria, intestinal parasites and other harmful microorganisms, which can cause waterborne diseases such as diarrhea, dysentery, and typhoid. Due to unsafe drinking water, along with poor sanitation and hygiene, are the main contributors to an estimated 4 billion cases of diarrhea disease annually, causing more than 1.5 million deaths, mostly among children under 5 years of age (Banks et al, 1992).

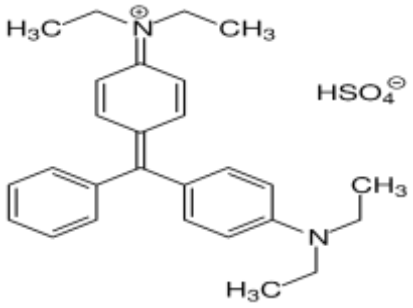
A number of low-cost adsorbents such as activated carbon prepared from different wastes like diatomaceous earth (Elemen et al, 2012), industrial waste products (Elizalde et al, 2003), bagasse fly ash (Hirata et al, 2002), clay mineral (Gambhir et al, 2012), biodegradable waste (Garg et al, 2015), hydrotalcite (Gupta et al, 2004), coffee grounds (Gupta et al, 2003), dusts (Gupta et al, 2007), kudzu (Kacha et al, 2003), 'waste' metal hydroxide sludge (Kadirvelu et al, 2003), agricultural waste (Kumar et al, 2001), dolomitic sorbents (Lazaridis et al, 2003), charcoal from extracted residue of coffee beans (Lee et al, 2017), bentonite and polyaluminum hydroxide (Nakamura et al, 2003) have been studied for adsorption of different dyes from solutions.

Removal of many dyes by conventional waste treatment methods is difficult since these are stable to light and oxidizing agents and are resistant to aerobic digestion. There are number of methods of dye removal from textile effluents include chemical oxidation, froth flotation, adsorption, coagulation etc. Adsorption is found to be the best process to treat dye wastewater. Previously only widely used adsorbents were in practice for treatment purposes but many researches are now conducted to use cheaply available natural materials. Although the adsorption of dyes over zeolite has been extensively investigated (Netpradit et al, 2003, Nevondo et al, 1999), only a few studies have been reported on adsorption of dye onto fly ash based zeolite (Peng et al, 2007, Srinivasan, 2013).

Many industrial solid wastes, such as fly ash and bottom ash contain silicon in abundance therefore these raw materials have been utilized for the production of mesoporous silica (Venkat et al, 2006). In spite of the exemplary work, the adsorption capacity of fly ash-derived mesoporous silica materials needs to be further enhanced for the practical application in industry.

Brilliant green is a water soluble basic triarylmethane dye which is used to colour the material like silk, wool, jute, leather, cotton, paper and other industries. In aquaculture, it acts as an anti-fungal, anti-bacterial and anti-parasitical agent. It has been classified as Class II health hazard, but still used in some countries because of its low cost. It is difficult to biodegrade and removes it from water bodies. It has been reported to cause carcinogenesis, mutagenesis, chromosomal fractures, and respiratory toxicity. Brilliant green is effective against Gram-positive bacteria.

The purpose of this study is to prepare Zeolite material for the removal of brilliant green dye from wastewater. Zeolite material was prepared from coal fly ash by hydrothermal treatment process. Batch experiments were designed for the sorption process, and the effects of temperature, pH value, initial concentrations of brilliant green and adsorbent dosages on adsorption were evaluated. The optimum condition was also discussed for brilliant green removal.



Scheme 1: Molecular structure of Brilliant Green

II. MATERIALS AND METHOD

2.1 Brilliant Green Dye

Brilliant green is anionic dye having chemical formula C27H34N2O4; MW, 482.62g/ mol-1; IUPAC name as [4-[[4-(diethylamino) phenyl]-phenylmethylidene] cyclohexa-2, 5dien-1-ylidene] diethylazanium; hydrogen sulfhate was supplied by Merck, India and used as adsorbate. A stock solution 1000ml was prepared by dissolving a weighed amount (1.0g) of brilliant green in one liter distilled water. Different concentrations were prepared by diluting the stock solution with suitable volume of distilled water and the natural pH of the stock solution was around 5.6. All the reagents used were of analytical grade. The concentration of dye was measured with a 1cm-path-length cell at a wave length (λmax) of 630 nm.

2.2 Fly Ash Collection and Adsorbent Development

A sample of fly ash was collected from H.E.G. Thermal Power Station, Mandideep (MP) India. It was in the form of small, spherical grayish black particles. The collected sample was sieved to a desired particle size ranges (150 µm). Sample was washed with distilled water five times to remove the adhering organic materials and then dried in an oven at 110 °C for 24 h, and finally stored in vacuum desiccator.

2.3 Zeolite Synthesis

The direct hydrothermal method was used with some modification for the synthesis of zeolites since it is fast, economic and less involving than the other fusion and the microwave methods as reported earlier. Mixture of NaOH and zeolite is taken in predetermined ratio of 1:2 and kept for fusion at 550ºC for 04 hours. After this fusion mixtures were washed with double distilled water and agitated for 15 hours on magnetic stirrer to wash off excess of alkali, filtered on whatmann filter paper and dried in oven for 04 hours at 100ºC and stored in desiccator before use.

2.4 Adsorption Studies

The adsorption was performed using the batch method. The equilibrium adsorption uptake and percentage removal of Brilliant Green from the aqueous solution q_e (mg/g) was calculated using the following relationship:

$$\text{Amount adsorbed } q_e = \frac{(Co-Ce)V}{W} (mgg^{-1}) \quad (1)$$

$$\%\ \text{removal } q_e = \frac{100(Co-Ce)}{Co} \quad (2)$$

Where C_o is initial adsorbate concentration (mg L^{-1}), Ce is equilibrium adsorbate concentration (mg L^{-1}), V is the volume of solution (L), W is the mass of adsorbent (g).

2.5 Adsorption Isotherms

The equilibrium data obtained in the present study were analyzed using Langmuir and Freundlich isotherm models. The rearranged Langmuir and Freundlich isotherm equations can be described as:

$$1/qe = 1/qm + (1/bqm)\ (1/Ce) \quad (3)$$

$$\log qe = \log K_f + 1/n \log Ce \quad (4)$$

2.6 Kinetic Studies

Intraparticle diffusion technique is used for identifying the mechanism involved in adsorption process. In order to investigate the mechanism of the Brilliant Green adsorption onto zeolite adsorbent, intraparticle diffusion based mechanism was studied. Kinetic studies were carried out in batch at 5 mg/l of initial dye concentration with a fixed dose of adsorbent dose of 5g/l at 30^0C and pH 5.0. After a fixed time interval the adsorbent was separated by filtration and the filtrate thus obtained was analyzed spectrophotometrically to determine the equilibrium concentration of the dye. The study of kinetics of adsorption explains the solute uptake rate at the solid-solution interface. The rate constant of adsorption of dyes on to zeolite (Kad) has been studied using the Lagergren first order rate equation:

$$\log (qe - qt) = \log qe - K_{ad}t / 2.303 \quad (5)$$

where qe is the amount of dye adsorbed at equilibrium, and qt is the amount of dye adsorbed at time t (mg/g).

III. RESULT AND DISCUSSION

3.1 Characterization of Adsorbent

The chemical composition of coal fly ash determined by X-ray fluorescence spectrometer is shown in Table 1. The result shows that the mineralogy of this CFA is very rich and it is class F fly ash. The sum of SiO_2, Al_2O_3 and Fe_2O_3 content in the CFA was found to be greater than 70%, while its CaO content was lower than 5%. Minor elements within the CFA were also identified by the XRF and the results reveal that trace elements like Sc, Ni, Cu, Sr, Rb, Zr, Nb are also present.

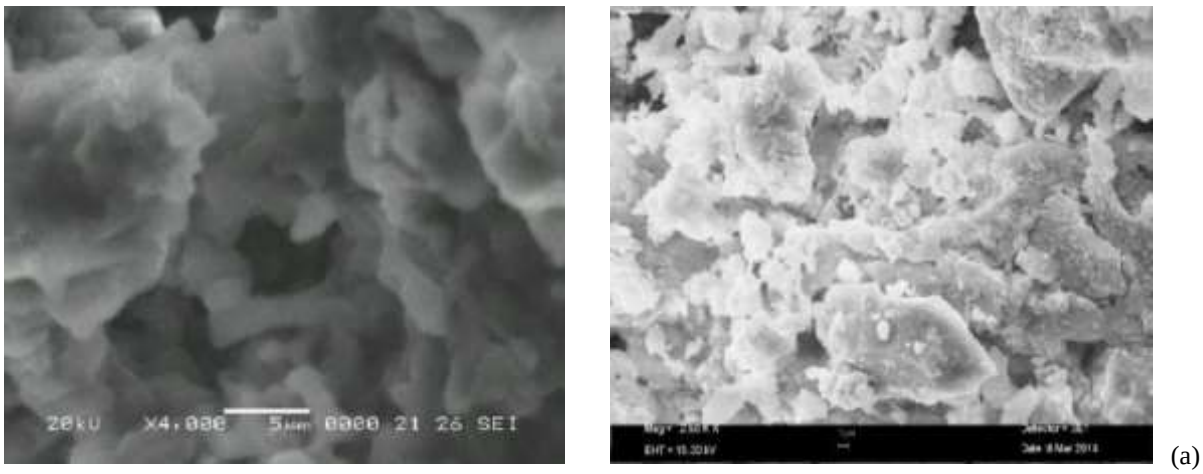
The results of SEM investigation of coal fly ash and zeolite are shown in (Fig. 1) which shows typical fly ash morphology and surface texture. Particles present in the fly ash are mostly sub angular and spherical in shape. The image also shows that the particles present in the fly ash are covered with relatively smooth grains of quartz, clusters of iron (Fe-oxide). SEM image confirms various type of particles of fly ash in raw form as well alkali activated fly ash has resulted into a significant transition in morphology from lumps to crystalline form which is attributed to chemical reaction between Si_4+, Al_3+, and Na+ ions and their nucleation.

The diffractogram (Fig. 2) reveals the X-ray diffraction pattern of fly ash for particle size ≤ 45 μm. It is seen that the fly ash consists mostly of mullite, quartz, hematite and a small amount of hematite and calcium oxide with large characteristic peaks of quartz (SiO2). The intensity of quartz is very strong with mullite that forms a chemically stable and dense glassy surface layer. The low calcium oxide intensity is characteristic of Class-F fly ash. It is observed that there is reduction in the silica and alumina contents associated with the crystalline particles of the fly ash due to its alkali activation. This can be attributed to the dissolution of the metal oxides and release of corresponding soluble ions Na+.

The infrared spectrum of fly ash (Fig. 3) reveals broad and weak peaks in the region of 4000-500 cm^{-1} associated with the functional groups that are on the surface of coal fly ash. The band which appears at 560 cm^{-1} is associated with octahedral aluminium present in mullite. In addition, bands appearing between 800-600 cm^{-1} are associated with tetrahedral vibrations formed which are known as secondary building units and fragments of alumino-silicate system. Band appearing at 2360 cm-1 could be attributed due to alkyl groups that are present in clay material of coal fly ash. Bands appearing at 800-1200 cm-1 and 450-550 cm^{-1} assign to asymmetric stretching mode and bending mode of T-O bond respectively. These bands are more or less dependent on the crystal structure. The mid region of infrared spectrum contains the fundamental framework vibrations of $Si(Al)O_4$ groupings. It is observed that there are significant changes in the intensities and the width of various bands due to interaction of fly ash with alkali. It can be noticed that there is an increase in intensity and broadness of the stretching frequency OH band at 3452 cm^{-1} after the treatment. This can be attributed to an increase in hydrated products due to the reaction between amorphous silicate and the alkali.

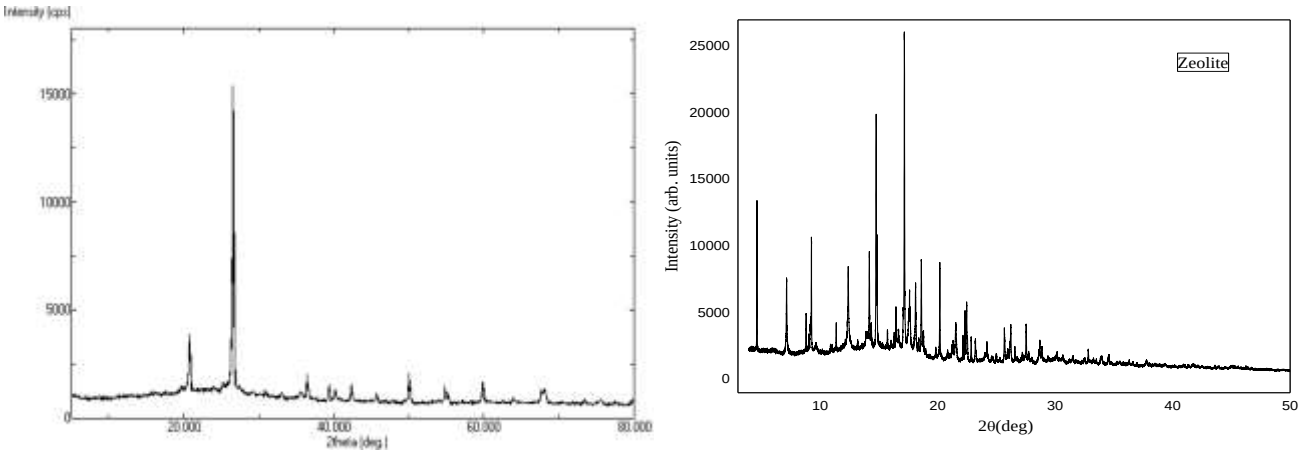
Table 1: Chemical constituents of the fly ash

Constituents	%Weight
SiO_2	55.26
Al_2O_3	22.75
Fe_2O_3	7.12
CaO	4.10
TiO_2	2.95
K_2O	2.14
P_2O_5	1.65
SO_3	1.58
Na_2O	1.23
MgO	0.63
LOI	4.10



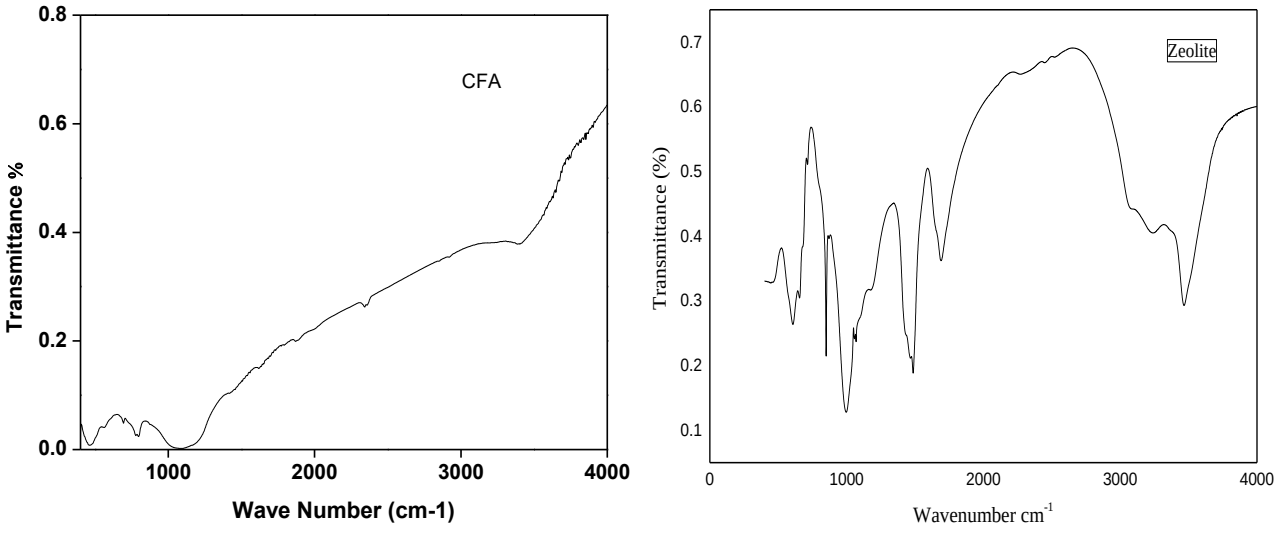
(b) (a)

Fig. 1: SEM image of (a) Coal fly ash (b) Zeolite



(a) (b)

Fig. 2: X-ray diffraction pattern of (a) Coal fly ash (b) Zeolite



(a) (b)

Fig. 3: FTIR of (a) coal fly ash (b) Zeolite

3.2 BATCH STUDIES

3.2.1 Effect of Contact Time

The effect of contact time was studied at Brilliant Green concentrations of 10 and 15 ppm with a fixed adsorbent dose of 5 g/l at 30±1°C. From the Fig.4,it is cleared that 95 % of the total amount of brilliant green uptake was found to occur in 120 minutes with 15 ppm dye concentration and thereafter no appreciable change occurred due to saturation of the active site which do not allow further adsorption to take place.

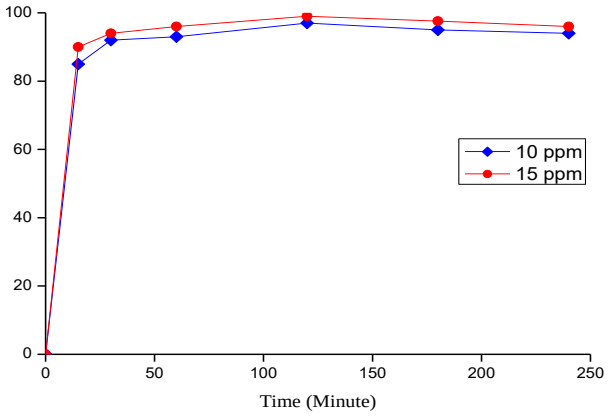


Fig.4: Effect of contact time on Brilliant Green dye adsorption

3.2.2 Effect of pH

The pH of the solution was found to influence the adsorption of the adsorbate on adsorbent. The effect of pH on the adsorption of Brilliant Green was evaluated at 30°C at different pH values in the range of 2–8 pH was adjusted by adding either 0.1M HCl or 0.1M NaOH.(Fig. 5) suggested that adsorbed amount increased with increasing pH value and an appreciable amount of adsorption occurred at pH 5.

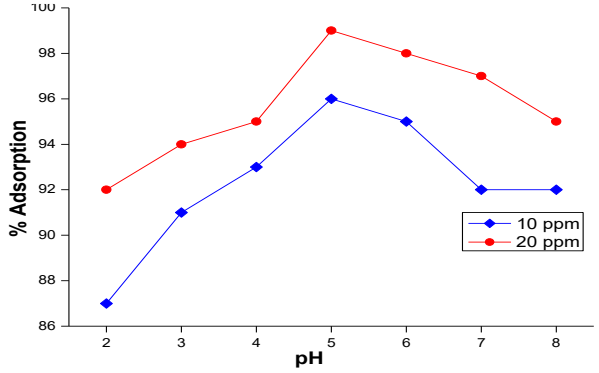


Fig. 5: Effect of pH on Brilliant Green dye adsorption

3.2.3 Effect of Amount of Adsorbent

In order to investigate the effect of mass of adsorbent on the adsorption of Brilliant Green, a series of adsorption experiments was carried out with different adsorbent dosage at initial concentrations of 10 and 15 ppm. The percentage removal of Brilliant Green increased with the increase in adsorbent initially from 5 g/l to 15, g/l. With the increase in the amount of adsorbent, the sites for adsorption increase initially. But on increasing it further the adsorption efficiency is reduced.Fig. 6 shows the effect of adsorbent dosage on the removal of Brilliant Green. This can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase in adsorbent dosage.

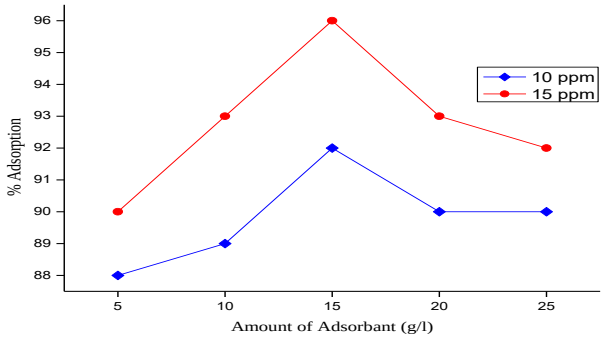


Fig. 6: Effect of adsorbent dosage on Brilliant Green dye adsorption

3.2.4 Effect of Initial Adsorbate Concentration and Temperature:

The effect of initial adsorbate concentration on the removal efficiency was investigated at temperatures of 30°,40° and 50°C (Fig.7). The experiments were carried out with fixed adsorbent dose of 15 g/l of activated adsorbent at pH 5. The increment in sorption capacity may be due to the increase of metal concentration which resulted in higher concentration gradient of the dye, thus leading to higher sorption capacity. Results indicating that uptake of Brilliant Green was favoured at high temperature.

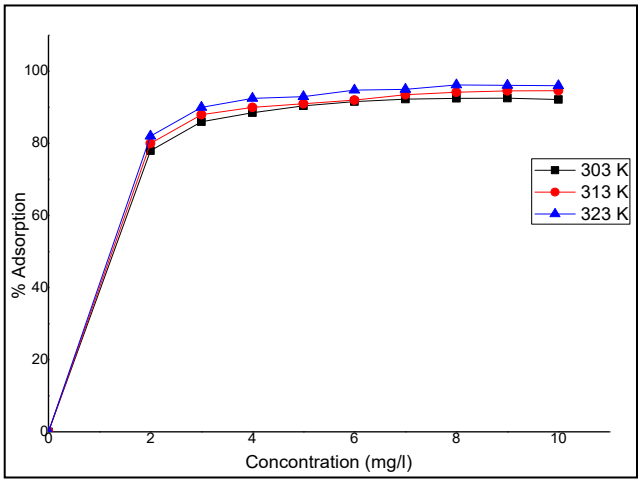


Fig. 7: Effect of adsorbate concentration and temperature on Brilliant Green dye adsorption

3.3 Adsorption Isotherms

The adsorption of Brilliant Green dye at equilibrium with increases in initial dye concentration at 30°C has been fitted in Langmuir model and Freundlich isotherm.

The results obtained on the adsorption of Brilliant Green were analyzed by the well-known models given by Langmuir and Freundlich.In Langmuir isotherm, values of 1/qe and 1/Ce were plotted for the adsorption of Brilliant Green (Fig. 8).The Langmuir constants, b and qm were calculated and the values of these were shown in Table 2.

Table 2: Freundlich and Langmuir isotherm parameters at 30°C

Freundlich parameters			Langmuir parameters		
K_f (mg/g)	1/n	R^2	q_m (mg/g)	b	R^2
4.8842	0.3905	0.9466	0.2411	1.5937	0.8621

The equilibrium adsorption data has also been fitted in the linear form of Freundlich isotherm model. logqe against log Ce, values were plotted for the adsorption of Brilliant Green which clearly showed that the data is fitted very well to the Freundlich model (Fig. 9). The calculated value of 1/n is less than 1, which suggests the favorable adsorption of dye onto the coal fly ash. The Freundlich constants, K_f and n were calculated from the best-fit lines and the values were given in Table 2.

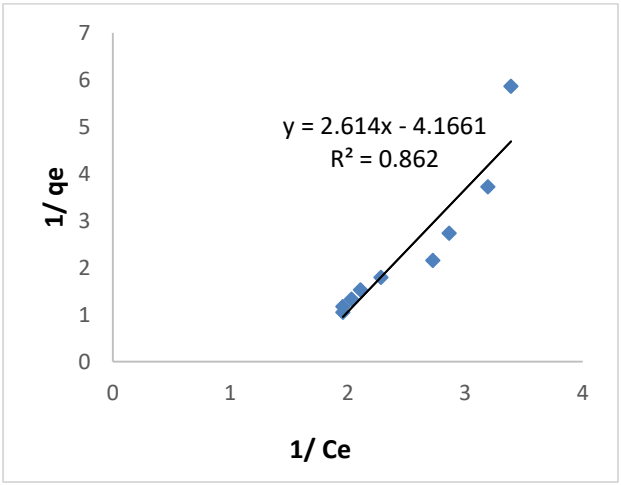


Fig. 8: Langmuir's plot of Brilliant Green dye

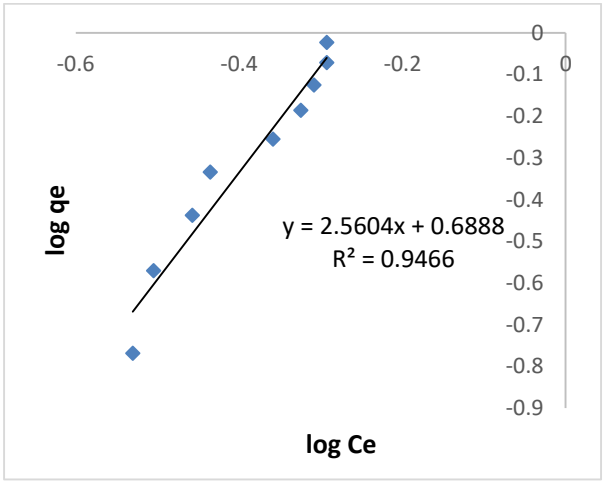


Fig. 9 Freundlich plot of Brilliant Green dye

3.4 Thermodynamic Parameters

Thermodynamic parameters were evaluated by using the data obtained from the adsorption isotherms**.** The change in standard free energy (ΔG^0), Enthalpy (ΔH^0) and entropy (ΔS^0) of adsorption for Brilliant Green was calculated by known methods and the values are given in Table 3. The negative free energy value indicates the feasibility of the process and spontaneous nature of adsorption. Positive enthalpy value indicates the process is endothermic in nature. Positive entropy value supports the affinity of the adsorbent material and feasibility of the system under consideration.

Table 3: Thermodynamic Parameters of Brilliant Green

ΔG^0 (KJ mole^{-1})	ΔH^0 (KJ mole^{-1})	ΔS^0 (KJ mole^{-1} K^{-1})
-1.174	10.960	0.041

3.5 Kinetic Studies

The graph (Fig. 10) obtained for log (qe − qt) versus time (t) in minutes exhibits straight lines and confirm the adsorption process to follow first order rate kinetics in each case. The Kad value calculated from slope of the plot (K_{ad}/2.303) is min^{-1}.

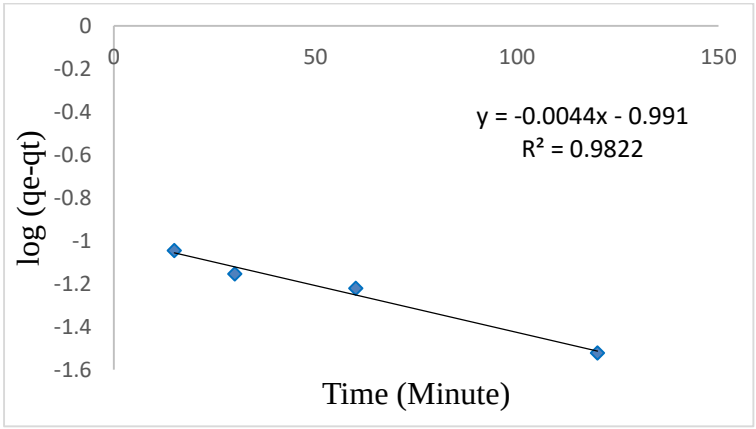


Fig. 10: Lagargren's plot of Brilliant Green dye adsorption

IV. CONCLUSION

The studies revealed that zeolite synthesized from coal fly ash can be fruitfully employed as adsorbent for the removal of Brilliant Green dye. The pH was found to be significant factor which affects the adsorption capacity of Brilliant Green. The removal of Brilliant Green dye is about 90 % at 40 mg/l with a dose of adsorbent of 15 g/l and pH 5.0 at 303 K. The optimum contact time was 120 min. The adsorption process was found to be of first order, physical and endothermic in nature. The adsorption data was analyzed by Langmuir and Freundlich models and fitted well. The fitness of Freundlich's model indicated the formation of multilayer coverage of the adsorbate on the outer surface of the adsorbent. The developed adsorbent is quite cheaper than commercially available activated carbons, while their performance is comparable.

REFERENCES

[1]. Aksu, Z. 2005. Application of biosorption for the removal of organic pollutants: a review, Proc. Biochem. 40: 997-1026.
[2]. Al-Ghouti, MA. Khrsisheh, MA. Allen, SJ. and Ahmed, MN. 2003. The removal of dyes from textile wastewater: a study of the physical characteristics and adsorption mechanisms of diatomaceous earth. J Environ Manage. 69: 229-238.
[3]. Allen, SJ. Gan, Q. Matthews, R. and Johnson PA. 2003. Comparison of optimised isotherm models for basic dye adsorption by kudzu. Bioresource Technol. 88:143-152.
[4]. Armagan, B. Ozdemir, O. Turan M. and Celik, MS. 2003. Clay Mineral Batch Process for Color Removal of Textile Wastewaters J. Environ. Sci. Hlth. Part A -Toxic Hazard Subst Environ.38 (10): 2251-2258.
[5]. Armagon, B. Turan, M. Celik, MS. 2006. Equilibrium studies on the adsorption of reactive azo dyes on the zeolite. Desalination. 170: 33-39.
[6]. Banat, IM. Nigam, P. Singh, D. and Marchant, R. 1996. Microbial decolorization of textile-dye containing effluents: A review. Bioresource Technol. 58: 217-227.
[7]. Banks, CJ. and Parinson, ME. 1992. The mechanism and application of fungal biosorption to colour removal from raw waters. J. Chem. Technol. Biotechnol. 54: 192-196.
[8]. Elemen, S. Kumabasar, EPA. and Yapar, S. 2012. Modeling the adsorption of textile dye on organoclay using an artificial neural network. Dyes and Pigments, 95: 102-111.
[9]. Elizalde Gonzalez, MP. Pelaez Cid, AA. 2003. Removal of textile dyes from aqueous solutions by adsorption on biodegradable wastes. Environ Technol, 24: 821-829.
[10]. Hirata, MN. Kawasaki, T. Nakamura, K. Motsumoto, M. Kabayama, T. Tamura and Tanada, S. 2002. J Colloid Inter Science, 254, 7-22.
[11]. Gambhir, RS. Vinod Kapoor, A. Nirola, R. Sohi and Bansal, V. 2012. J. Hum Ecol, 37 (2), 103-109.
[12]. Garg, AM. Mainrai, VK. Bulasara, Barman, S. 2015. Chemical Engg. Commun. 202 (1), 123-130.
[13]. Gupta, VK. Suhas, I. Ali and Saini, VK. 2004. Ind Engg Chem Res, 43, 740-1747.
[14]. Gupta, VKD. Mohan, S. Sharma and Sharma, M. 2003. Sep SciTechnol, 35, 2097-2113.
[15]. Gupta, VKR. Jain and Varshney, S. 2007. J Haz. Materials, 142, 443-448.
[16]. Kacha, SZ. Derriche, S. Elmaleh, 2003. Water Environ Research, 75, 15-20.
[17]. Kadirvelu, KM. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani and Pattabhi, S. 2003. Bioresource Technol, 87, 129-132.
[18]. Kumar, PN. Mal, Y. Oumi, K. Yamanaa and Sanoc. T. 2001. Journal of Materials Chemistry, 11(12), 3285–3290.
[19]. Lazaridis, NK. Karapantsios TD. and Georgantas, D. 2003. Water Research, 37, 3023-3033.
[20]. Lee, YR. JT. Soe, SQ. Zhang, JW. Ahn, MB. Paek. and WS. Ahn, 2017. Chemical Engineering Journal, 317, 821–843
[21]. Nakamura, TM. Hirata, N. Kawasaka, S. Tanada, T. Tamura and Nakahon, Y. 2003. EnvironSciTechnol, 38, 555-562.
[22]. Netpradit, SP. Thiravetyanand S. Towprayoons, 2003. Water Research, 37, 763-772.
[23]. Nevondo, TS. Cloete, TE. Water SA, 1999. 25 (2): 215-220.
[24]. Peng, LZ. Liuxue, 2007. Sep Pur Technol, 58 (1), 32-39.
[25]. Srinivasan, V. 2013. Indian Journal of Science and Technology, Suppl. 6, 4777-4782.
[26]. Venkat, SM. Indra, DM. Vima, CS. 2006. J. of Env. Manage. 74 (3), 647-652.