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EXPLORING THE ADSORPTION POTENTIAL OF COAL FLY ASH AND ZEOLITE FOR REMOVAL OF ACID VIOLET 19 DYE AND ITS PHYTOTOXICITY ASSESSMENT

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ABSTRACT

The present study deals with the effect of coal fly ash and zeolite on Acid violet 19 dye removal from aqueous solution under different experimental conditions such as exposure time, adsorbent dose, pH and temperature. The maximum adsorption of Acid violet 19 dye was observed at pH2 with optimum adsorbent dose 1.2g at 60 ^{0}C. Zeolite synthesized from coal fly ash showed significant removal of Acid violet 19 dye from aqueous solution as compared to coal fly ash. Equilibrium data were examined by Langmuir and Freundlich isotherms. Langmuir isotherm appeared as the best fit model with maximum 0.88 mg/g adsorption capacity. The phytotoxicity study revealed that growth and biochemical components of fenugreek seeds were significantly increased with zeolite treated dye solution in comparison to coal fly ash. Hence, zeolite can be used as a low cost, effective and economically feasible adsorbent for removal of acid violet 19 dye for treatment of industrial effluent.

KEY WORDS : Acid violet 19, Coal fly ash, Phytotoxicity, Zeolite

INTRODUCTION

Electricity is an essential requirement for all facets of our life and it has been recognized as a basic human need. The electricity infrastructure and generation are important for a developing nation like India, with a population of 1.2 billion in an area of 3.29 million Km^2. Most of the electricity is producedin India by the coal based thermal power plants (Tiewsoh *et al.*, 2019). India having the fifth largest coal reserves in the world, and coal has been proven the most economical form of electricity production in India. More than eighty five thermal power plants in India are producing approximately 120 million tonnes coal fly ash/year which may increase to 442 million tonnes/year by 2035 (Jambhulkar *et al.*, 2018) India holds fourth position in global ranking for production of fly ash as a waste by-product after Russia, USA and China (Senapati, 2011). The fly ash contains many toxic substances which accumulate in air, water and soil (Misaelides, 2011) and causes various health related disorders in human-beings such as asthma, bronchitis, fibrosis, skin allergy and cancer (Donaldson and Borm, 1998). The disposal of huge quantity of fly ash is an arduous task for thermal power plants. Several approaches have been used for application of fly ash to reduce its deleterious impact on environment. The conversion of fly ash into zeolite has wide applications as molecular sieve, catalyst and adsorbent (Breck, 1974).

Dyes are colored ionized aromatic organic material (Abd-Elhamid *et al.*, 2020). It has been estimated that approximately 1.6 million tonnes of dyes are annually used in the industries and around 10-15% of the dyes are lost in the effluent during the dyeing operations (Tan *et al.*, 2015). The industries such as textile, paper, printing, cosmetic, plastic, paint, leather and pharmaceutical etc. are the malefactors for polluting the water resources by inadvertent discharge of dye contaminated wastewater directly into the water bodies (Hou *et al.*, 2017; Kumar *et al*., 2018). The colored effluent not only create environmental and aesthetic problems, but also pose a serious threat to human health (Garg *et al.,* 2015). Synthetic dyes adversely affect human health due to their mutagenic, carcinogenic, genotoxic and immune suppression effects (Choi *et al.,* 2014). To resolve the challenge of water contamination by the discharge of dyes into water bodies, various physical and chemical methods have been applied such as coagulation, photo-catalytic degradation, electrochemical treatment, reverse osmosis and ozonation etc (Ma *et al*., 2019; Zhou *et al*., 2019). The above mentioned methods have some drawbacks such as long operation time, high operational cost, intensive energy requirement and unable to completely remove the dyes (Kumar *et al*., 2019). Adsorption is superior method as compared to other techniques for effluent treatment in terms of cost, ease of operation and simple procedure (Gupta *et al.,* 2013). Fly ash is locally available at zero cost, reusable and biodegradable in nature and it can be utilized as a low-cost efficient adsorbent for the treatment of industrial effluents. The objective of the present investigation is to develop a way to manage the fly ash waste into an eco-friendly cleaner material which can be used in effluent treatment process. The current research is focused on the use of coal fly ash and zeolite prepared from coal fly ash for the removal of Acid violet 19 dye by adsorption due to their large surface area and ion exchange capacity (Sayal *et al*., 2012). Fenugreek (*Trigonella foenum-graceum* L.; family Leguminosae) is an annual plant. Fenugreek leaves and seeds are consumed due to its medicinal properties such as anti-diabetic, lowering of blood glucose and cholesterol level, anti-microbial and anti-carcinogenic properties. To the best of our knowledge, no report is available in literature till date on the effect of coal fly ash and zeolite treated Acid violet 19dye solution on the growth and biochemical parameters of fenugreek. Therefore, present study was conducted to compare the adsorption efficiency of coal fly ash and zeolite for decolorization of Acid violet 19 dye from aqueous solution and its impact on fenugreek seeds.

MATERIALS AND METHODS

Coal flyash was collected from NTPC Dadri, Gautam Buddh Nagar, Uttar Pradesh as a raw material. Acid violet 19, an anionic dye was procured from Sigma Aldrich, India. All the chemicals used in this study were of analytical grade.

Zeolite synthesis

The zeolite was synthesized by hydrothermal activation of 20 g coal fly ash at 100 ^{0}C in 160 ml of 3.5 mol/L NaOH solution for 24 h. The zeolitic material was repeatedly washed with deionized water to remove excess sodium hydroxide until the washing water had pHS10, then it was dried at 50 ^{0}C for 24h (Henmi, 1987).

Preparation of the dye stock solution

The stock solution of Acid violet 19 dye (1000 ppm) was prepared and it was diluted to produce desired concentrations. A calibration curve was plotted by analyzing different concentrations of Acid violet 19 dye solution by using UV-Visible double beam spectrophotometer at 541 nm.

Adsorption studies

Batch adsorption study was conducted to check the efficiency of coal fly ash and zeolite prepared from coal fly ash as an adsorbent for decolorization of Acid violet 19 dye from aqueous solution. The effect of different parameters such as contact time (30-120 min), dye concentration (20-80 ppm), adsorbent dose (0.3-1.5 g), pH (from pH 2 to 10) and temperature (20-80 ^{0}C) was investigated for the removal of Acid violet 19 dye. In the batch adsorption study, 100 mL of Acid violet 19 dye solution of different concentrations (20, 40, 60 and 80 ppm) were placed in four different Erlenmeyer flasks (250 mL capacity) with different amount ofcoal fly ash and zeolite (0.3, 0.6, 0.9, 1.2 and 1.5g) respectively. The mixture was placed in an incubator shaker at 120 rpm until equilibrium was observed to be attained. The conical flasks were withdrawn at regular time interval and analysis of the sample was made by following standard procedure. The pH of the solution was maintained by using 0.1N HCl and 0.1N NaOH solution.

Removal efficiency of dye was calculated by the following formula:

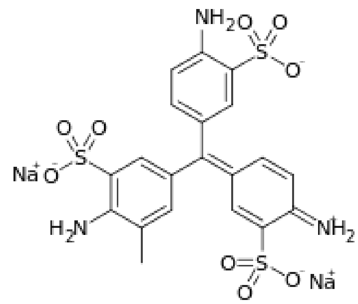
Removal of Acid violet 19 dye (%) = $C_o - C_t / C_o \times 100$

Where C_0 and C_t were initial and final concentrations of Acid violet 19 dye at time t in mg/L in the sample, respectively.

Adsorption isotherm

Two isotherm models were used to interpret

Table 1. Details of acid violet 19 dye used in the experiment

Dyestuff	Acid violet 19, Acid Fuchsin
Appearance	Dark green
IUPAC Name	Disodium 2-amino-5-[(Z)-(4-amino-3-sulfonatophenyl)(4-iminio-3-sulfonato-2,5-cyclohexadien-1-ylidene)methyl]-3-methylbenzenesulfonate
Empirical Formula	$C_{20}H_{17}N_3Na_2O_9S_3$
Molecular Weight	585.538 g/mol
Molecular Structure	
λ_{max}	541 nm

sorption equilibrium in the present study. One hundred milliliters of Acid violet 19 dyes (20-80 mg/l) was mixed with five different adsorbent amount. The adsorption capacity and equilibrium solution concentrations were evaluated with suitability of the isotherm.

Langmuir isotherm

The Langmuir isotherm model speculates that adsorption process takes place in a monolayer mode. It also explains that adsorption energy is consistent throughout adsorbed layer on adsorbent surface at a constant temperature (Bharathi and Ramesh, 2013).

Langmuir equation was expressed as:

$$C_e/q_e = 1/q_e K_1 + C_e/q_m$$

where q_e (mg/g) was Acid violet 19 dye amount adsorbed at equilibrium, q_m (mg/g) is dye amount adsorbed, C_e is equilibrium dye concentration (mg/l) and K_1 is Langmuir constant related to binding strength of dye on zeolite.

Freundlich isotherm: Freundlich isotherm explains distribution of solute molecules between aqueous and solid phases at equilibrium. This isotherm assumes an exponential disparity in energy of surface-active sorption site and reduction in adsorption heat is logarithmic (Ng *et al.,* 2002).

The Freundlich equation:

$$\text{Log } q_e = \log K_f + 1/n \log C_e$$

where, Freundlich constants such as K_f and n were adsorption capacity and intensity of adsorption, respectively. The value of n reflected nature of process: (1). n = 1, a linear process (2). n < 1, a chemical process and (3). n > 1, a physical process.

Phytotoxicitystudy

Effect of Acid violet 19 dye before and after treatment with coal fly ash and zeolite was studied on the growth and biochemical parameters of fenugreek (*Trigonella foenum-graecum*) seeds.

Seed germination test : The empty and undeveloped seeds of fenugreek (*Trigonella foenum-graecum*) were discarded by floating in tap water. Seeds of fenugreek were thoroughly washed with tap water to remove dirt and dust for 5 minutes. The seeds were surface sterilized with 10:1 distilled water/ bleach (commercial NaOCl) solution for 5 minutes for inhibition of microbial infection and then washed 6 -7 times with distilled water. Fenugreek seeds were soaked in Acid violet 19 dye solution before and after the treatment with coal fly ash and zeolite prepared from fly ash for 4 hours respectively. The filter paper was placed in sterilized petri - dishes (20 cm diameter) and fenugreek seeds which were soaked in dye solution before and after treatment with fly ash and zeolite were transferred into petridishes. The petridishes were covered with sterilized polythene bags and kept in a Seed Germinator for 8 days under 70% relative humidity at 25±2^{0}C with 12h photoperiod following guidelines of ISTA (2008) in three replicates with completely randomized block design.

Germination percentage: Total number of seeds germinated / Total number of seeds taken for germination x 100

Different growth characteristics such as radicle and plumule length and vigour index were determined in control and treatment after 8 days of seedling growth by the following methods:

Seedling length: The radicle and plumule length of fenugreek seedlings were measured with a measuring scale and values were expressed in centimeters.

Vigour index: Vigour index of the fenugreek seedlings was estimated according to the formula: Vigour index = Total seedling length (mm) x germination percentage (Abdul Baki and Anderson, 1973).

Determination of pigment content: The seedlings (100 mg) of control and treatment were grounded with 80% acetone and pigments were extracted and centrifuged. The absorbance of supernatant was recorded at 663 and 646 nm by using UV-visible spectrophotometer. The amount of total chlorophyll (Chla+b) was calculated by the method of Lichtenthaler (1987).

Estimation of sugar and protein contents: The determination of total soluble sugars was done following the procedure of Hedge and Hofreiter (1962). Fenugreek seedlings (0.1 g) were homogenized in 5 ml 95% (v/v) ethanol. After centrifugation, 1 ml supernatant was mixed with 4 mlanthrone reagent and heated on boiling water bath for 10 min. The absorbance was recorded at 620 nm after cooling. The amount of sugar was determined by the standard curve prepared from glucose.

Fenugreek seedlings (10 mg) were homogenized with 1 mL of 1N NaOH for 5 min at 100 ^{0}C. 5 ml of alkaline copper reagent was added to it and mixture was allowed to stand at room temperature for 10 minutes and 0.5 ml of Folin-Ciocalteau reagent was added in the test tube. The absorbance of the solution was measured at 650 nm after 30 min and the amount of protein was calculated with reference to a standard curve of bovine serum albumin (Lowry *et al*., 1951).

Statistical analysis

Treatments were arranged as randomized block design with three replications. Data were statistically analyzed using analysis of variance (ANOVA) by using SPSS software (Version 16 SPSS, US). The standard error of mean was calculated for presentation with Tables and Figures and treatment mean was analyzed using Duncan's multiple range test (DMRT) at $P < 0.05$.

RESULTS AND DISCUSSION

In the present study, effect of coal fly ash and zeolite synthesized from coal fly ash for removal of Acid violet 19 dye was studied by changing different parameters such as contact time, initial dye concentration, pH, adsorbent dose and temperature. The phytotoxic effect of Acid violet 19 dye and coal fly ash and zeolite treated dye solution was also studied on the growth and biochemical parameters of *Trigonella foenum-graecum.*

Effect of contact time: Batch experiments were carried out to study the effect of coal fly ash and zeolite on various concentrations of Acid violet 19 dye (20-80 mg/l) under different exposure periods (30-120 minutes). Results showed that the adsorption capacity of coal fly ash and zeolite increased rapidly with increasing contact time for the first 90 minutes (Figure 1). The 90 minute was considered as the optimum exposure period for Acid violet 19 dye removal for both of the adsorbents. From the Figure 1, it can be observed that dye removal efficiency decreases with increasing dye concentration and adsorption process was more effective at low concentration of the dye solution, i.e. 40 ppm (Garg *et al*., 2015). Zeolite exhibited better adsorption capacity for Acid violet 19 dye as compared to coal fly ash (Fungaro *et al*., 2009).

Effect of adsorbent dose: The different amount of coal fly ash and zeolite (0.3 g, 0.6 g, 0.9g, 1.2 g and 1.5 g) was taken in the experiment to evaluate their adsorption capacity for Acid violet 19 dye. The

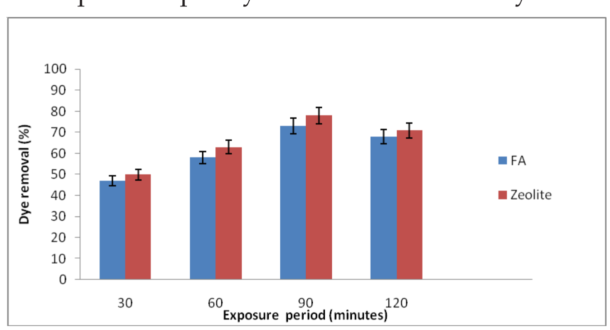


Fig. 1. Adsorption of Acid violet 19 dye by coal fly ash and zeolite at different exposure period.

increase in the rate of adsorption of Acid violet 19 dye was observed with increase in the adsorbent amount and exposure period (Fig. 2). The adsorption capacity of coal fly ash and zeolite showed the following trend: 1.2g > 0.9> 1.5g > 0.6g > 0.3g. The results indicated that zeolite was effective in removal of Acid violet 19 dye from aqueous solution in comparison to coal fly ash. It might be due to more surface area and availability of more adsorption sites on the zeoliteas compared to coal fly ash (Anbia and Salehi, 2012).

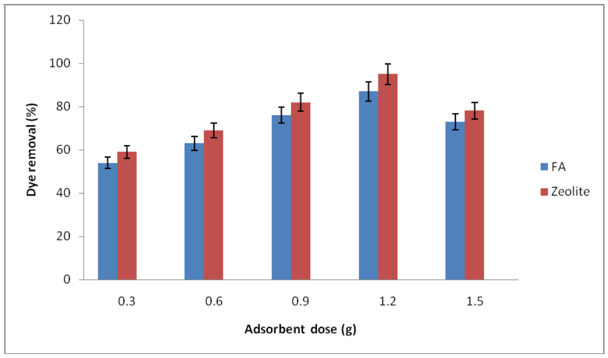


Fig. 2. Adsorption of Acid violet 19 dye by different adsorbent dose.

Effect of pH: The percentage of Acid violet 19 dye adsorption by coal fly ash and zeolite at different pH is shown in Fig. 3. The pH is significant operating parameter in the adsorption process. It was observed that at low pH, more dye molecules were protonated and get adsorbed on the surface of coal fly ash and zeolite. At pH 2, maximum Acid violet 19 dye removal 86 and 94% were observed with coal fly ash and zeolite, respectively for an initial dye concentration of 40 mg/l.

Effect of temperature: The adsorption of Acid violet 19 dye on the coal fly ash and zeolite was carried out with initial dye concentration (40 mg/l) at different

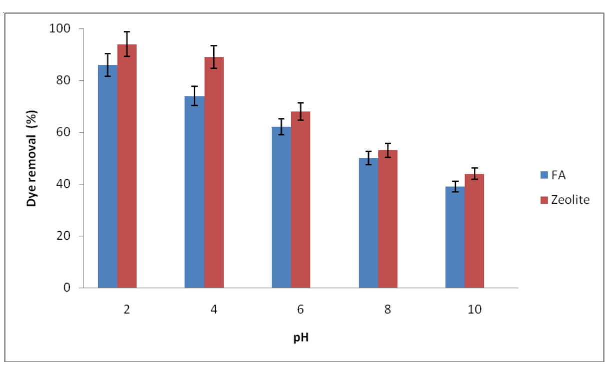


Fig. 3. Adsorption of Acid violet 19dye by coal fly ash and zeolite at different pH.

temperature. The dye adsorption increased on the coal fly ash and zeolite with increase in temperature from 20 to 80 °C (Fig. 4). This was due to the increased surface activity at high temperature and reflected the adsorption of Acid violet 19 dye on coal fly ash and zeolite obeyed an endothermic process. Maximum removal of Acid violet 19 dye72 and 79% was observed with coal fly ash and zeolite, respectively at 60 ^{0}C.

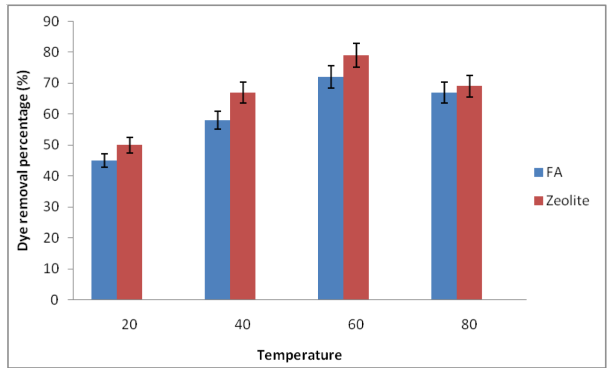


Fig. 4. Adsorption of Acid violet 19 dye by coal fly ash and zeolite at different temperature.

Adsorption isotherm: Adsorption isotherm exhibited how dye molecules were dispersed between liquid and solid phases at a constant temperature under equilibrium. The isotherm models provide valuable information on adsorption mechanism, surface property and adsorbent capacity. The Langmuir isothermassumes that there is a homogeneous distribution of active sites on the surface of the adsorbent, which adsorb a single molecular layer of adsorbate molecules with no interaction between the adsorbed molecules. Freundlich isotherm model is an exponential equation, which applies to heterogeneous system with interaction between adsorbed molecules and is not restricted tothe formation of a monolayer. This model assumes that as the adsorbate concentration increases, the concentration of the adsorbate on the adsorbent surface also increases and correspondingly that sorption energy exponentially decreases on completion of the sorption centers of anadsorbent. Hence, isotherm data of Acid violet 19 dye adsorption on zeolite was assessed by using Langmuir and Freundlich models (Table 2).

In the present study, Langmuir isotherm reflected better fitting model than Freundlich as observed by high correlation coefficient (R^2 = 0.8993). It showed monolayer coverage of Acid violet 19 dye on zeolite adsorbent (Wang *et al.,* 2017).

After calculation by the equation, Langmuir constants showed following values: q_m= 0.88 mg/g and k = 9.022 mg^{-1} and Freundlich constants were K_f = 2.49802 and n = 1.75 and R^2= 0.8369.

Phytotoxicity study

Growth parameters: The phytotoxicity test was conducted to analyze the impact of Acid violet 19 dye onfenugreek seeds. The significant differences were observed in different treatment for all the parameters studied, i.e. seed germination and growth characteristics such as seedling length and vigour index of fenugreek seeds (Table 3). In control, 97% seed germination was observed whereas Acid violet 19 dye (40 ppm) treated *Trigonellafoenum-graecum* seeds showed only 32% germination (Singh *et al*., 2015). The significant increase 91 and 158% in fenugreek seed germination was reported in dye solution treated with coal fly ash and zeolite, respectively over Acid violet 19 dye. The radicle and plumule length were3.6 and 9.5cmsin control which were significantly reduced to 0.4 and 3.1 cms in Acid violet 19 dye solution. Zeolite treated dye solution showed significant increase in radicle and plumule length in comparison to coal fly ash treated dye solution. The vigour index of fenugreek seeds showed the following trend: Control > zeolite treated dye solution > coal fly ash treated dye solution > Acid violet 19 dye.

Biochemical parameters: Pigments are the essential component for the growth and development of plants and can determine health status of plants. Acid violet 19 dye solution adversely affected pigment content and showed highest suppression in total chlorophyll content 57% as compared to control. Sugar and protein contents were negatively affected as 65 and 56% reduction in sugar and protein contents were observed in fenugreek seedlings respectively when exposed to Acid violet 19 dye solution in comparison to control (Table 4). All the biochemical components such as total chlorophyll, sugar and protein contents in fenugreek seedlings showed the following trend: Control > zeolite treated dye solution >coal fly ash treated dye solution > Acid violet 19 dye.

Performance of zeolite as compared to other adsorbent : The efficiency of prepared zeolite for Acid violet 19 dye removalwas compared with other adsorbents are given in Table -5. The dye removal efficiency was used for comparison. Acid violet 19 dye removal efficiency is in agreement with earlier reports, suggesting that Acid violet 19 dye can be smoothly adsorbed on zeolite. It shows thatzeolite prepared from coal fly ashcan be cost- effective and promising adsorbent for Acid violet 19 dye.

Table 2. Isotherm constants for acid violet 19 dye adsorption by zeolite

Isotherm	Equation	Plot	Parameters	Value
Langmuir	$C_e/q_e = 1/q_e$ K_1 '+ C_e/q_m	A plot Ce/qe versus Ce showed straight line of slope 1/qm and an intercept of 1/(Kaqm)	qm (mg/g) K (l/mg) R^2	0.88 9.022 0.8993
Freundlich	Log q_e= log K_f +1/n log C_e	K_f and 1/n values were evaluated from intercept and slope of linear plot of lnqe versus lnCe, respectively	1/n K_f (mg/g) R^2	1.75 2.49802 0.8369

Table 3. Effect of acid violet 19 dye before and after treatment with coal fly ash and zeolite on seed germination and growth parameters of *Trigonellafoenum-graecum*

Treatment	Seed germination (%)	Radicle length (cms)	Plumule length (cms)	Vigour index
Control	96.67 ± 0.41[a]	3.6 ± 0.14[a]	9.5 ± 0.36[a]	12664
Acid violet 19 dye (40 mg/l)	32.33 ± 1.08[c]	0.40 ±0.07[c]	3.1 ± 0.32[c]	1132
Fly ash treated dye solution	61.70± 1.1[b]	2.2 ± 0.20[b]	6.4 ± 0.39[b]	5304
Zeolite treated dye solution	83.33 ± 1.47[a]	3.1 ± 0.31[a]	8.1 ± 0.19[a]	9333

Data are means ± standard error of three independent experiments with three replicates. Values followed by different letters show a significant difference at P < 0.05 significant level between treatments according to the ANOVA and Duncan's multiple range test.

Table 4. Effect of acid violet 19 dye before and after treatment with coal fly ash and zeolite on the biochemical components of *Trigonellafoenum-graecum*

Treatment	Total chlorophyll content (mg g^{-1} FW)	Sugar content (mg g^{-1} DW)	Protein content (mg g^{-1} FW)
Control	2.13 ± 0.23^a	3.09 ± 0.68^a	14.51 ± 1.32^a
Acid violet 19 dye (40 mg/l)	0.92 ± 0.02^d	1.08 ± 0.10^c	6.32 ± 0.75^c
Fly ash treated dye solution	1.30 ± 0.19^c	2.17 ± 0.20^b	11.95 ± 0.58^b
Zeolite treated dye solution	1.83 ± 0.23^b	2.76 ± 0.11^b	13.42 ± 0.98^a

Data are means ± standard error of three independent experiments with three replicates. Values followed by different letters show a significant difference at $P < 0.05$ significant level between treatments according to the ANOVA and Duncan's multiple range test.

Table 5. Comparison of acid violet 19 dye removal efficiency by various adsorbents

Dye	Adsorbent	Dye removal efficiency (%)	References
Acid violet 19	Laccase modified zeolite	93	Kalkan *et al*. (2015)
	NaOH-modified fly ash	91.96	Gao *et al.* (2016)
	Zeolite 5 A	94.94	Ahmedzeki and Kamil (2017)
	LTA-type zeolite	71.6	Xu *et al*. (2014)
	Dalbergiasissoo saw dust	50.07	Sharma *et al*. (2019)
	Polyaniline-Fe_2O_3 magnetic nano-composite	98.5	Patil and Shrivastava (2015)
	Zeolite prepared from coal fly ash	94	This study

CONCLUSION

The results revealed that the removal of Acid violet 19 dye by using zeolite is a simple, economically feasible and environmentally-benign process. The phytotoxicity test on fenugreek seeds showed the growth promoting nature of coal fly ash and zeolite treated dye solution as compared to the toxic Acid violet 19 dye. The present investigation may be useful in fabrication of economically viable treatment system by utilization of zeolite for the removal of Acid violet 19 dye from industrial effluent.

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