Adsorption of reactive blue 21 by flyash and treated flyash, a low cost adsorbent

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Abstract

Wastewater from textile industry contains various pollutants including a high content of organic matter, additives, surfactants and dyes. Dye has obtained notoriety as hazardous substances, because most of them are toxic. These dyes are harmful for environment and aquatic life. Also, dyes are resistant to biodegradation. Thus, the study was performed to investigate the removal of colour for specified reactive dye (RB 21) using different types of easily available adsorption media like flyash, treated flyash, sawdust, rice husk, waste apricot, clay mineral. Fly ash gives good removal of dye from synthetic wastewater. The effect of various parameters such as pH, temperature, adsorbent dose and concentration has been investigated in the batch experiments. Dye removal efficiency for RB 21 reached up to 33% & 88% at lower concentration, and then decreased to less than 6% & 77% at higher concentration for RFA and TFA. The amount of dye adsorbed decreases with increase in the concentration of solution from 2.5-50 mg/l at room temperature, indicating the process to be highly dependent on the initial dye solution concentration.

Keywords: Adsorption, flyash, treated flyash, sawdust, rice husk, waste apricot, clay mineral.

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Introduction:

Dyes are a type of organic compounds that can provide bright and lasting colour to other substances. Dyes are considered to be particularly dangerous organic compounds for the environment [1]. Hence, the removal of dyes from wastewater is essential to prevent continuous environmental pollution. Various methods have been used for the treatment of dye-containing wastewater, including biological treatment, adsorption, chemical oxidation, coagulation, and reverse osmosis. Adsorption is an effective method for the separation of effluent pollutants and effluents treatment [2]. The phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or a solid resulting into a higher concentration of the molecules on the surface is called adsorption. The substance thus adsorbed on the surface is called the adsorbate and the substance on which it is absorbed is known as adsorbent. As activated carbon adsorption is highly effective at removing dyes and pigments, it is often too expensive to be used in developing countries; in such cases, the use of low-cost adsorbents, such as clay minerals, flyash [3, 4], waste apricot [5], rice husk, sawdust [6], fungi [7] and waste materials from agriculture [8].

One potential approach is the use of coal flyash as a low-cost adsorbent. Fly ash is a by-product producing during the combustion of coal in the electricity generation process [9]. Disposal of fly ash has become an increasing economic and environmental burden [10]. In this paper, the study is carried out for the removal of dye Reactive Blue 21 (RB21) using low cost adsorbents raw flyash and treated flyash.

2. Materials and method:

2.1. Adsorbent

Raw coal flyash (FA) used in this study was collected from coal-burning thermal power plant at Koradi thermal power station, Nagpur District, Maharashtra, India. It was washed with tap water several times to avoid impurities. The fly ash powder was dried in the electric oven (Make Tempo) at 105°C for at least 24 hours and kept over fused calcium chloride in the desiccators, just prior to

use. Raw flyash which was dried at 378K was separated manually by passing the flyash over the standard size mesh no.45 (354μ) molecular sieves (Make Endecotts). The chemicals used in this study were of analytical grade (Merck).

2.1.1. Treatment of flyash

20g of raw flyash was mixed with 50mmol of $MnSO_4$ (Merck) in 70ml aqueous solution and maintained at controlled temperature (80°C) using water bath for 20min. under magnetic stirring. 33mmol of $KMnO_4$ (Merck) prepared in 350ml aqueous solution was added gradually on the above reaction mixture maintaining the temperature at 80°C continuing with magnetic stirring. After complete addition of $KMnO_4$, the reaction mixture was kept for stirring at 80°C for 15 min. Then, it was kept for cooling at room temperature. Washing was done several times by centrifugation (Cooling centrifuge REMI) using distilled water and then, the treated flyash was dried at 100^0C for overnight.

2.2. Characterization

The surface area, pore size and total pore volume of the FA and TFA were measured through N_2 adsorption-desorption method Brunauer-Emmett Teller (BET) (Micrometrics). The surface morphology and quality of both the adsorbent samples was characterized by a High Resolution Scanning Electron Microscopy (HR-SEM) (JEOL, JXA-840). The slurry pH of both the adsorbents was measured using bench top pH meter (Eutech). The mineralogical compositions of both the adsorbent were measured using Desktop powder X-ray Diffractometer (XRD) (Rigaku).

2.3. Adsorbate

The adsorbate used in this study was reactive blue 21(Dystar) provided by textile industry, Ludhiana and it was used for adsorption studies without any further purification. Its structure was shown in (Fig.1). The synthetic wastewater was prepared by dissolving reactive blue 21 in deionized water (Milli-Q) for different concentration (2.5, 10, and 50) mg/L .The UV-visible spectrum (Shimadzu) of dye (Fig.2.) was initially determined and identified the adsorption wavelength (λ_{max}). The molecular formula and molecular weight of RB 21 is $C_{41}H_{23}N_{14}O_{14}S_5Cl_1Na_4Cu_1$ and 1126.70936, respectively.

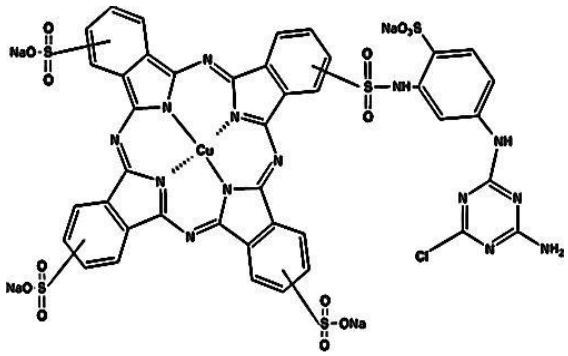


Fig.1. Chemical structure of RB 21

2.4. Adsorption study

Batch experiments were carried out to measure the adsorption characteristics of RB 21 on FA and TFA. Prior to their use, both the adsorbents were dried in oven at 105°C for 1 hr. to eliminate traces of moisture. A series of 250ml graduated conical flasks containing 100ml solution of each concentration (2.5, 10, and 50) mg/L of known amount (1.0g) of FA and TFA was prepared. Its adsorption isotherm was recorded. The mixture was kept in shaking incubator (Tempo) at 100rpm for various times (2-160 min.) to determine equilibrium time at different temperature 288, 298 and 308 K. After agitation, the suspension was separated by filtration using 0.45 μm membrane filter paper (Whatmann). The residual concentration of dye solution was determined at 665 nm using a standard calibration curve prepared at the corresponding maximum wavelength using a UV-Visible spectrophotometer. Langmuir and Freundlich isotherm were applied to evaluate the adsorption capacity of FA and TFA.

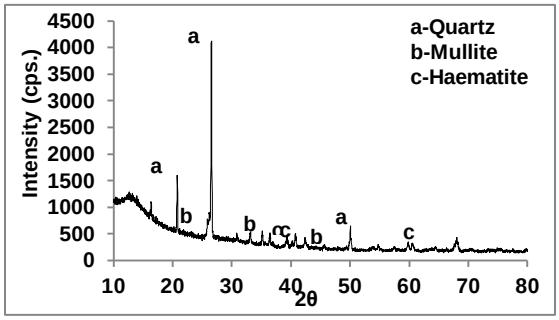
3. Results and discussions

3.1. Characterization of adsorbents and adsorbate

The specific surface area of FA obtained from the N_2 equilibrium adsorption isotherm (BET) were found to be 1.2530 m^2/g. TFA shows drastic increase in BET surface area, due to the increasing of amorphous formation. The specific surface area of TFA is 69.5820 m^2/g, respectively.

XRD shows that raw FA is heterogeneous in nature, consisting of a mixture of glassy particles with various crystalline phases such as quartz (SiO_2), mullite (Al_2O_3), and some oxides Fig.2 (a). The powder diffraction pattern of FA readily indexed to the hexahedral crystalline structure of quartz (Joint Commission on Powder Diffraction Standards [JCPDS] card no.89-1961, lattice parameter: a=4.921Å, c=5.416 Å) and for mullite & haematitite (Fe_2O_3) it resemble with rhomohedral crystalline structure (JCPDS card no.88-0826, lattice parameter: a=4.76Å, c=12.99 Å) and (JCPDS card no.89-2810,

lattice parameter: a=5.04 Å, c=13.75 Å). The XRD pattern of TFA shows decrease in intensity of quartz and mullite because the amorphous component of TFA increases as shown in Fig.2 (b). Presence of Fe_2O_3 and other oxides was not observed in XRD pattern due to its lower concentration. MnO_2 having cubic crystalline structure (JCPDS card no.73-1539, lattice parameter: a=4.53Å, b=9.27 Å, c=2.866 Å).



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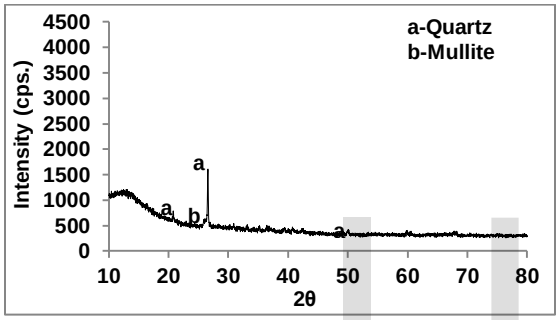
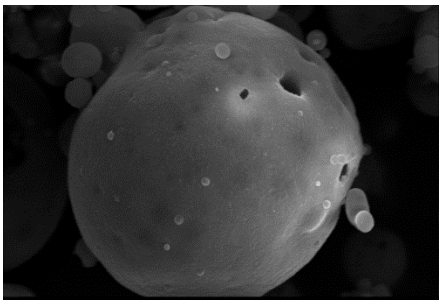


b

Fig.2 (a & b): Powder diffraction pattern of RFA and TFA

Flyash particles are generally spherical in shape. Fig.4 shows the SEM image of RFA and TFA. A marked change in surface morphology was observed, when the TFA is compared with the raw FA. The raw FA comprises smooth spherical particles, whereas the TFA shows rougher surface with full of holes Fig.3(a & b).



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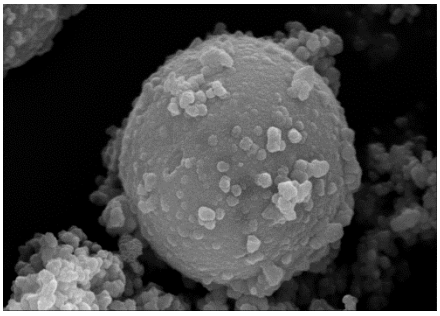

b

Fig.3 (a & b): SEM images of RFA and TFA

3.2. Dye adsorption studies

3.2.1. Effect of pH

The effect of initial pH on the adsorption process was investigated. The effect of pH on the adsorption of RB-21 by raw FA and TFA was studied by varying the solution pH over a range of 2.5 to 11.5 using 0.1 N NaOH and HCl solutions at 288K. The results in Fig 4. indicate that for both adsorbents the removal was at a maximum at the initial pH of 2.5 (~ 71%) for FA and (~ 100%) for TFA, respectively. At alkaline pH, the removal efficiency decreased drastically. Since, the pH of an aqueous dye solution is about 7.0, the following experiments were made without the pH adjustment of the dye solutions.

3.2.2. Effect of contact time

To evaluate the effect of contact time between dye and adsorbent, the agitation time was varied between (2-160) min for both raw FA and TFA. The results are shown in Fig 5. It was observed that equilibrium adsorption time for both the adsorbent are same and the equilibrium is achieved within (90-120) min.

3.2.3. Effect of initial dye concentration

The adsorption capacity of raw FA and TFA for reactive dye RB 21 was determined at different initial dye concentrations. It was observed that dye removal efficiency for RB 21 reached up to 33% & 88% at lower concentration, then decreased to less than 6% & 77% at higher concentration for RFA and TFA. The results represented in Fig. 6. shows that the amount of dye adsorbed decreases with increase in the concentration of solution from 2.5-50 mg/l at room temperature, indicating the process to be highly dependent on the initial dye solution concentration.

3.3. Adsorption studies

The calculation to determine the percent adsorption of the dyes was made according to the equation:

$$\% \text{ adsorption} = (C_0 - C_e)/C_0 \times 100$$

The percentage removal of the dye and the amount adsorbed (mg/g) were calculated by the following relationship:

$$Q_e = (C_0 - C_e)/m$$

Langmuir developed a theoretical equilibrium isotherm relating the amount of gas adsorbed on a surface to the pressure of the gas. The linear form of Langmuir isotherm equation is given as:

$$1/Q_e = C_e/Q_0 + 1/Q_0K_L$$

C_e/Q_e was plotted against C_e using linear regression analysis as shown in Fig7 (a) .The constants Q_0 and K_L were determined from the intercept and slope of the linear plots, respectively. The Q_0 from Langmuir isotherm were 0.536, 0.287, 0.255 and 0.189 mg/g while the values of K_L were 0.374, 0.420, 0.512 and 1.14 L/mg, respectively.

Freundlich developed an empirical model which can be applied to non-ideal adsorption on heterogeneous surfaces [11] as well as multilayer adsorption. The Freundlich model [12] equation is expressed as

$$Q_e = K_F C_e^{1/n}$$

The linear logarithmic form of Freundlich is given by the following equation:

$$\ln Q_e = \ln K_F + 1/n \ln C_e$$

K_F can be defined as an adsorption or distribution co-efficient and represents the amount of adsorbate adsorbed on an adsorbent for a unit equilibrium concentration.

lnQe plotted against $\ln C_e$ as shown in Fig 7(b). From the Freundlich isotherm the K_F values was found to be 0.238, 0.154, 0.121 and 0.095 mg/g and the values of adsorption intensity were 0.188, 0.339, 0.463 and 0.554, respectively.

where ,C_0 = initial concentration of the dye in (mg /L);

C_e = equilibrium concentration of dye in (mg/ L);

m = mass of adsorbent in (g /L);

Q_e = amount of dye adsorbed per gram of adsorbent (mg/g);

Q_0 = maximum monolayer coverage capacity (mg/g)

K_L = Langmuir isotherm constant (L/mg);

K_F = Freundlich isotherm constant (mg/g);

n = adsorption intensity

Equilibrium adsorption data of RB 21 onto RFA and TFA reveals that, RFA fitted to Langmuir isotherm i.e. monolayer adsorption process and TFA fitted to Freundlich isotherm i.e. multilayer adsorption process.

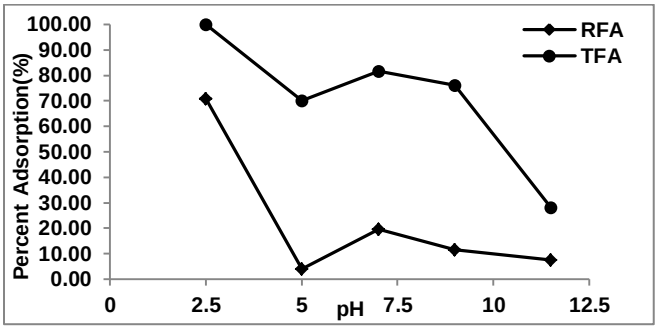

Fig 4: Effect of solution pH on dye adsorption on RFA and TFA (Initial dye concentration 10mg/L, contact time 90 minute, dose 1.0 g/100ml, temperature 298K)

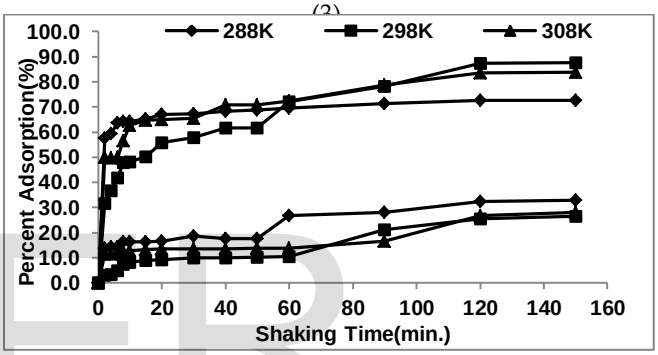

Fig 5: Effect of temperature on adsorption of RB 21 by RFA and TFA. [Initial dye concentration range (2.5-50) mg/l, contact time 90 minute, dose 1.0g/100ml]

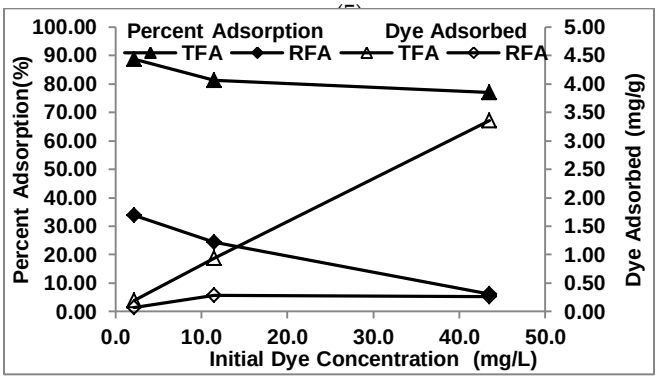

Fig.6: Effect of initial dye concentration on percent adsorption and dye adsorption capacity using RFA and TFA. (Initial dye concentration (2.5-50) mg/l, contact time 90 min, dose 1.0 g/100ml, temperature 298K)

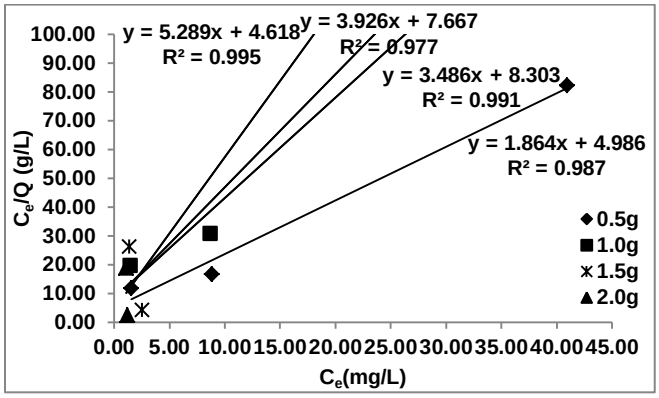

Fig 7(a). RFA showing Langmuir adsorption isotherm [Initial dye concentration range (2.5-50) mg/l, contact time 90minute, temperature 298K]

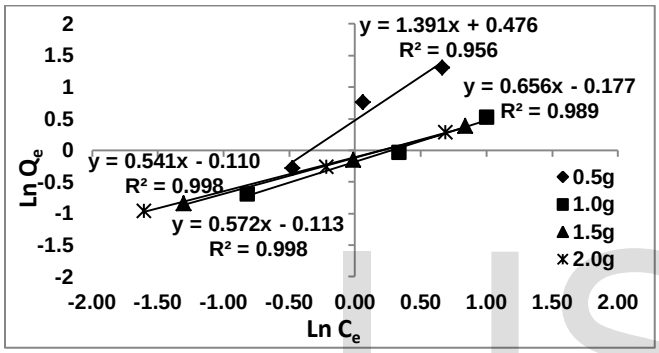

Fig 7(b). TFA showing Freundlich adsorption isotherm [Initial dye concentration range, (2.5-50) mg/l, contact time 90minute, temperature 298K]

Conclusion:

- This study shows that the dye removal efficiency for RB 21 reached up to 33% & 88% at lower concentration, and then decreased to less than 6% & 77% at higher concentration for RFA and TFA indicating the process to be highly dependent on the initial dye solution concentration.
- The equilibrium data follows Langmuir isotherm for RFA and Freundlich isotherm for TFA.
- The study demonstrates that TFA is a potential and active low-cost adsorbent for removal of reactive dye from its aqueous solution.

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