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Insight into equilibrium kinetics and isotherm Studies on Sorption of Alizarin Red S Dye onto Ca $(OH)_2$ Modified Fly Ash

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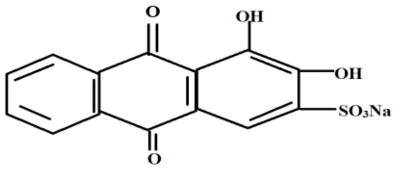
ABSTRACT
Dye stuff industries produces a bulk quantity of waste which is disposed off into lakes and streams without any prior treatment and which has a significant negative impact on human being and aquatic habitat . Researchers were employing various treatment methodologies for the removal of the organic and inorganic waste. Research is going on to develop a low cost adsorbent which could be used for removing different sorts of dyes stuff which is discharged from the industrial effluent outlet. In this study, removal of Alizarin Red S Dye by using $Ca(OH)_2$ treated fly ash powder as an adsorbent. Operating parameters employed in this study such as adsorbent dosage, pH, and agitation speed. Langmuir Isotherm fits well with the experimental data and Pseudo-Second Order Kinetics is obeyed in this study.

Introduction
Environmental Pollution has increased due to the dynamic usage of the dye consumed in the textile industry. Different sorts of dyes used without prior treatment. They were disposed off into the lakes, streams and water bodies. These Dyes not only create pollution for the aquatic fauna and flora but also has a significant negative impact on human being. More than 10,000 various kinds of dyes are commercially available which finds its use in many industrial processes such as textile, paper and plastics, leather dyeing, pharmaceutical, printing, etc [1-3]. Under aerobic conditions, many dyes can decompose into carcinogenic aromatic amines which can be a cause serious health hazards to humans and animals [4,2]. Moreover, dyes cause allergy, dermatitis, skin irritation and even cancers in humans [5].

Alizarin Red S (ARS) $C_{14}H_6Na_2O_7S$(Sodium Alizarin Sulphonate3,4-Dihydroxy-9,10-dioxo-2-anthraquininonesulfonic acid sodium salt C.I No: 58005) is a anthroquinone derived dye and the sodium salt is obtained by direct sulphonation of alizarin ,which finds its application in histochemical staining and various other applications [6].



Chemical Structure of Alizarin Red S Dye

ARS were used to mark Japanese flounder *Paralichthys olivaceus* (T.) [7]. The dye is also used as an antidepressant drug and various pharmaceutical formulations [8]. It is also applied as an electrochemical indicator for the recognition of saccharide. In the field of drug delivery also it has some potent application.ARS dye showed sub lethal effects on Baltic cods and larvae[9].Baume and Derichsweiler employed intraperitoneal injections of a 2 percent of ARS dye , and it proved fatal to monkeys[10].

Adsorption could be probable alternative for the recent development in the waste water treatment research and application .This employs a wide application and advantages rather than the conventional techniques which are currently available. Low Cost Technology is an urgent need for the sustainability of the process. Industrial Waste and agricultural waste could be an alternative source of sorbent by means of which remediate the problem.

The main components of fly ash, a pozzolanic material are silicon dioxide, alumina, and iron oxide. Fly ash has some potent application for building materials which results in reusability of the generated fly ash[11]. In Fly ash Sio_2 is present abundantly and contains some unburned carbon also. Researchers have been reported on fly ash for the removal of dyestuffs from textile effluent, heavy metals[12-20],arsenic compounds[20,21] .In this work removal of anionic dye from aqueous solution were studied using $Ca(OH)_2$ modified Fly ash. Fly ash is also used for the development of geoplymers[22,23].The effect of various operating parameters such as adsorbent dose, initial solution pH and agitation speed of solution on Alizarin Red S adsorption was studied by batch adsorption studies. The most widely used adsorption isotherm models like Langmuir, and Freundlich were employed to study the equilibrium data. Kinetics of the adsorption process was examined by fitting the experimentally obtained equilibrium data with the kinetic models, viz. pseudo first order, and pseudo-second-order.

Materials & Methods
Adsorbent: Preparation
The fly ash used for the experiment was first obtained from a coal based power plant from Durgapur, West Bengal, India. It was washed repeatedly with double distilled water to remove all dust and soluble impurities, which was then followed by drying at 343K for 24h. The dried fly ash was the suspended in 10% calcium Hydroxide $Ca(OH)_2$ solution and the suspension was autoclaved at 10 psi for 15min. The alkali solution was filtered

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off after the pre-treatment and the fly ash was washed until the pH of the wash was close to neutral. The treated fly ash was then dried at 343K for 24h. After drying, the adsorbent was used in all experiments[24].

Preparation of Adsorbate Solutions

Alizarin Red S (ARS) used in this study was commercial grade (CI: 58005,MF: $C_{14}H_6Na_2O_7S$,MW:364.24 λ_{max} :594nm) and was used without further purification . Fresh stock solution (500 mgL^{-1}) was prepared by dissolving accurately weight quantity of the said dye in double –distilled water. An experimental dye solution of different concentration was prepared by diluting the stock solution with desired volume of double- distilled water .The initial solution of the pH was adjusted with 0.1 M HCl and 0.1 M NaOH solution by using a digital pH Metre (Eutech Instruments, Singapore).

Batch Experiments

The batch experiments were carried out in 250 ml glass stoppered Erlenmeyer flasks with a working volume of 100ml, with an initial dye concentration of 50 mgL^{-1}. A fixed amount of adsorbent was added to the solution. The flasks were agitated at a constant speed of 140 rpm for 240 minutes (4hrs) in an incubator shaker (Model Innova 42, New Brunswick Scientific, Canada) at 303±1 K. The influence of various process parameters like pH (2.0, 4.0, 6.0, 8.0, 10.0), adsorbent dosage (0.5, 1, 2, 3, 4 gL^{-1}) and Agitation Speed (100,140,180,220 rpm) were calculated during the current study. To study the residual dye concentration in the solution, samples were taken out from the flask at predetermined time intervals. The remaining dye concentration in each flask after a specified time of the experiment was analysed by using UV-Vis spectrophotometer (Tech Comp UV2310 Spectrophotometer). The amount of dye adsorbed per unit adsorbent (mg dye per g adsorbent) was calculated according the mass balance on the dye concentration using Eqn.(1):

$$q_e = \frac{(C_i - C_e)V}{m} \qquad (1)$$

Where q_e is the solid phase Conc. of adsorbate at equilibrium (mg/g), C_i is the initial dye Concentration (mgL^{-1}), C_e is the equilibrium dye Concentration in Solution (mgL^{-1}), V is the volume of the solution (L), and m is the mass of the adsorbent (g).

Now for calculating the percentage removal (%) of dye from the solution the following equation can be used.

$$Removal(\%) = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (2)$$

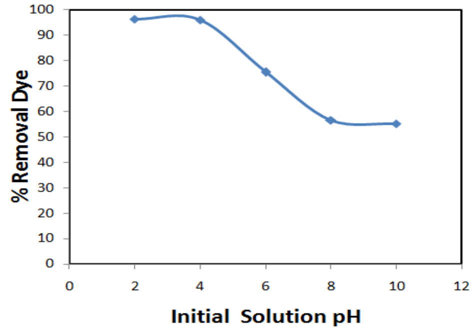
Where C_i is the initial dye Concentration (mgL^{-1}) and C_e is the equilibrium dye Concentration in solution (mgL-1)

All the adsorption experiments were performed in triplicate and the average values were used in data analysis.

Results and discussion

Effect of pH:

The initial solution pH is a significant operating parameter for adsorption study Fig. 1 shows the effect of the pH on the adsorption of ARS on adsorbent. The dye uptake was decreased as the pH of the solution increased. The decrease in the uptake values at low pH i.e. at pH 3 was attributed due to the decrease in ARS dissociation which led to lower concentration of anionic dyes. This could be explained on the basis of the lower extent of protonation of amino groups at high pH. ARS was first dissolved and the sulfonate groups of AR dissociate and were converted into anionic dye ions. Under acidic conditions sulfonate groups combined with H+ which decreased the adsorption capacity of ARS. So, in acidic conditions ARS gives best removal .Similar trend of result also observed by [25,26].



Effect of adsorbent dosage:

Biosorbent dose is also an influencing operating parameter. The influence of adsorbent dosage on ARS sorption by TFA was studied in the range of 0.5- 4 g. The percentage of removal of dye from the aqueous solution commencing at 90 % up to 97 % .Fig 1 elucidates that when the dose increased from 0.5 to 1 g the percentage removal of dye is maximum and when the dose is further augmented up to 4 g. there is no significant removal is observed from the obtained data. This phenomenon could be due to the more number of active sites present in the adsorbent and saturation could be due to the aggregation which would lead to decrease in total surface area of the adsorbent and increase in diffusional path length .Therefore, in the following experiment, adsorbent dose was fixed at 1 g(27).Similar trend of result was also showed by some earlier researchers.

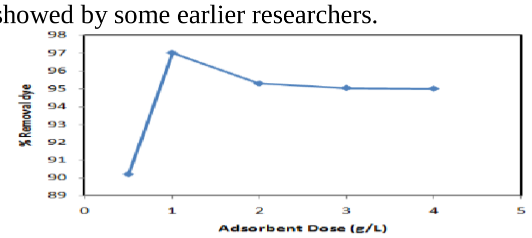


Fig 2 .Effect of Adsorbent Dose

Effect of agitation Speed:

Agitation speed was also studied in this present work. During adsorption the agitation speed was varied from 100 rpm to 220 rpm using predetermined quantity (1gm)of Treated fly ash and fixed amount of ARS solution of 50mgL^{-1} in an Incubator shaker (Model Innova42, New Brunswick Scientific, Canada).The initial and final concentrations were measured using UV/Vis Spectrophotometer(Model TechCompUV2310). Fig 2 shows that when the agitation speed is increased percentage removal of the dye was observed to decrease this phenomenon could be due to the higher centrifugal force. When the adsorbent experiences a higher centrifugal force the dye molecules which is attached in the surface of the adsorbent might be loosely bound and desorbed in the solution and finally decreased the percentage removal. Similar trend was observed and reported by researchers [28].

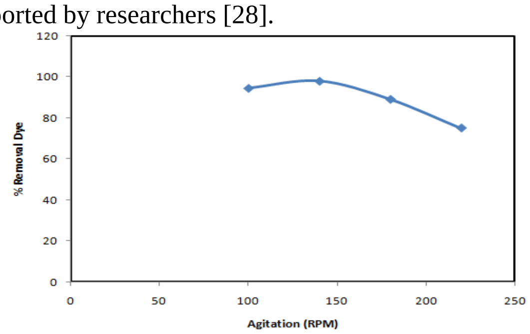


Fig 3.Effect of Agitation Speed

Isotherm Studies:

In the present study, the Langmuir, and Freundlich isotherm models were used to explain the equilibrium of the biosorption data obtained from the experiment. The equilibrium relationship between the adsorbate and adsorbent is explained by the adsorption isotherm. [29,30] .The Langmuir sorption isotherm elucidates that the uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules and is commonly expressed

$$\text{Langmuir: } \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (3)$$

Where q_e (mgg^{-1}) and C_e (mgL^{-1}) are the solid phase and liquid phase concentration of the adsorbate at equilibrium respectively ,q_m (mgg^{-1}) is the maximum adsorption capacity , and K_L (Lg^{-1}) is the adsorption equilibrium constant . The constants K_L and q_m can be determined from the slope and intercept of the plot between C_e/Q_e and Ce.

The Freundlich isotherm is applicable to non ideal adsorption on heterogeneous surfaces and the linear form of the isotherm can be represented as:

$$\text{Freundlich: } \log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (4)$$

where q_e is the equilibrium dye concentration on adsorbent (mg g^{-1}), Ce is the equilibrium dye concentration in solution (mg L^{-1}), K_F (mg g^{-1}) (Lg^{-1})$^{1/n}$ is the Freundlich constant related to sorption capacity and n is the heterogeneity factor. K_F and 1/n are calculated from the intercept and slope of the straight line of the plot log q_e versus log C_e.

The Langmuir and Freundlich Isotherm were employed for the sorption of ARS onto $Ca(OH)_2$ modified Fly Ash at 30°C are represented in Fig 4 and 5.The Langmuir and Freundlich constants calculated from the isotherm at 30°C with the correlation coefficients .From the calculated value it was observed that Langmuir model fits well with experimental data of the ARS removal by $Ca(OH)_2$ treated fly ash adsorbent. The experimental result shows that adsorption of ARS on modified FA follows Langmuir Model. The fitting of Langmuir Isotherm to experimental data at all temperature studied confirms that sorption is monolayer.

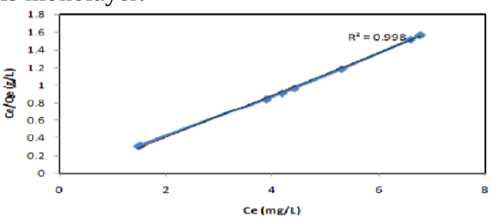


Fig 4. Langmuir Isotherm curve

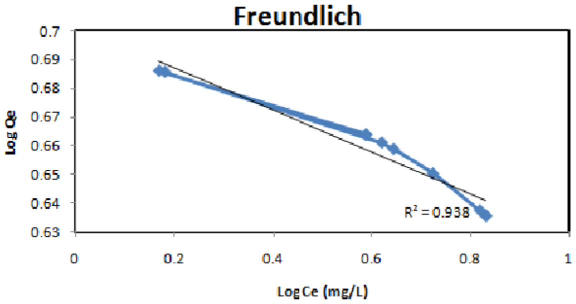


Fig 5. Freundlich Isotherm Curve

Kinetic Modelling:

To decipher the kinetics of the adsorption process, the pseudo first order (31,32)pseudo – second order (31,33), were employed. Pseudo first order equation is represented below:

$$Pseudo - first\ order: \log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

Pseudo –Second Order Kinetic Model

The linear form of Pseudo second order kinetic model can be expresses as follows

$$Pseudo - second\ order: \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

The kinetic data fitted well with the pseudo second order kinetic equation.Fig.6 shows that the experimental values showed linearity and R2 >0.999.The best correlation provided by the pseudo second order suggests that chemical sorption involving forces or sharing of electrons between adsorbent and adsorbate might be a significant.

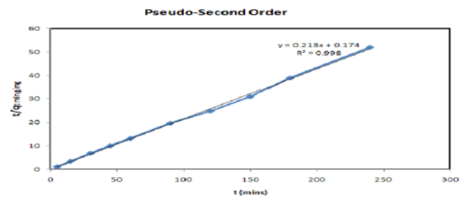


Fig 6. Pseudo –Second Order

Conclusion:

The present study indicates the application of alkali treated fly ash as a potent adsorbent for the removal of wastes bearing ARS .The sorption was governed by low pH and it is found that at pH3. The adsorption isotherms best fitted with Langmuir at all temperatures. The adsorption data gives good agreement with the pseudo-second order kinetic model. The results confirmed that the low cost easy available fly ash may be an effective for the treatment of effluent and dyestuff industries.

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