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ADSORPTIVE REMOVAL OF ERIOCHROME BLACK T (EBT) DYE FROM AQUEOUS SOLUTION USING CANE SUGAR BAGASSE AS BIOADSORBENT

By

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ABSTRACT

Textile effluent contains huge quantities of toxic chemicals and high level of chemical oxygen demands, which gets directly discharged into natural water bodies, thus contaminating the water quality. These effluents required prior treatment before being discharged into natural aqueous systems. In the present study, a low cost, highly efficient, eco-friendly adsorbent cane sugar bagasse from an industrial waste raw material will be used for the removal of eriochrome black t from aqueous solution. Parameters that influence the adsorption process such as contact time, initial dye concentration, dosage adsorbent, temperature, ph, activation time and adsorption studies will be studied in batch experiments. The experimental data will be analyzed using adsorption isotherm models freundlich and langmuir. Kinetics study will be carried out to see between pseudo-first order model and pseudo-second order model which is more suitable. The thermodynamic parameters will also be calculated, so that a conclusion will be drawn to ascertain whether cane sugar bagasse is a good adsorbent for the removal of color from textile waste water or not.

Keyword: Erichrome Black T, Cane Sugar, Bagasse, Adsorbent, Isotherm.

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INTRODUCTION

Dyes are synthetic aromatic water soluble organic substances with complex molecular structure and they are widely used for coloration in different industries like textile, paint, paper, plastic, food and cosmetics. Most of the dyes are toxic, carcinogenic and even mutagenic (Crini, 2006; Aksu, 2005). The removal of dyes from colored effluent is one of the major environmental concerns. Treatment of dye effluents is a difficult process because dyes have various synthetic origin and they contain complex aromatic molecular structure which make them more stable and more difficult to be degraded (Abdel-Ghani, *et al.,* 2007).

During the past decades, dyes have substantially ravaged aquatic environments and human health. Indeed, approximately 15% of the total dyestuff (over 7 x 10^5 tons is produced worldwide annually) is lost during the dyeing process in different textile industries and comes out with their waste water (Dutta, *et al.,* 20014). Therefore, effective removal of hazardous dyes from polluted water has become a critical point to be resolved. A number of techniques have been adopted to remove dyes, such as chemical precipitation, aerobic and anaerobic microbial degradation, ion exchange membrane separation, electrochemical treatment flocculation, reverse osmosis and adsorption (Li, *et al.,* 2015b, 2016). In comparison with other techniques, adsorption could be considered as an effective, attractive and promising process owing to its ease of operation, simplicity, suitability to treat concentrated dye wastes, selectivity, wide ranging availability and inexpensive nature (Li, *et al.,* 2015a).

In recent years, many adsorbents prepared on the basis of agricultural wastes and by products such as sugarcane bagasse (Zhang *et al.,* 2011), Luffa cylindrical fibres (Kesraoui *et al.* 2016), pineapple leaf (Rahmat, *et al.,* 2016) and sunflower seed hull (Hameed 2008) have been reported and applied for the removal of ionic and nonionic dye molecules from water. In recent papers, the utilization of agricultural byproducts as bioadsorbents was widely discussed in terms of capacity of pollutant uptake, isotherm and kinetic models and thermodynamic aspects, revealing that the solution pH, the nature of the dye and the chemical composition of adsorbents greatly affect the adsorption phenomenon (Mo'denes *et al.,* 2015).

Regarding the great diversity of cheap, environmentally benign and abundant agricultural by products, other efficacious bioadsobents could be considered as interesting for the uptake of hazardous pollutants from aqueous solutions. So, even if agricultural wastes have no remarkable industrial and commercial use, cane sugar could be regarded as a potential low cost bioadsorbent (Maaloul *et al.,* 2017).

EBT is chosen as model dye because it is hazardous, carcinogenic and toxic. Indeed, it is well known that EBT (sodium1-[1-hydroxynaphthylazo]-6-nitro-2-naphthol-4-sulfonate) is a typical mono-azo dye. EBT is widely used in textile, paper, printing, food and pharmaceutical industries, as well as in research laboratories (Gautam *et al.,* 2015).

Musa and Abdullahi, (2022) investigated the adsorption of Alizarin Red S from aqueous solution by base activated typa graa (*T. latifolia*) (ACT-TG) using batch system under controlled conditions. The adsorbent surface was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) methods and the point of zero charge (PZC). The kinetic data was best described by pseudo-second order models. For optimization purpose the adsorption parameters including effect of contact time, adsorbent dosage, initial concentration and pH was studied and the optimum adsorption capacity was found to be 46.61 mg/g. the isotherm for the adsorption process was also modelled and evaluated and the data generated fitted well the Freundlich isotherm model relative to other models tested. It was estimated through the study that the adsorption rate is positively affected by increase in dose of ACT-TG, dye initial concentration, contact time, pH and temperature. In the study Van't Hoff's plot was used to determine thermodynamic quantities of the adsorption process including ΔS (5.5862 J/molK), ΔH (-4.9001 kJ/mol) and ΔG (-6.419 to 6.734 kJ/mol). The results indicated that the adsorption process were feasible and spontaneous. Therefore, the base activated typha grass can be a potential adsorbent for the removal of hazardous dyes from wastewater.

EXPERIMENTAL METHODS

Materials

All solvent to be utilized for this study will be of analytical grade and commercially available. EBT will be purchased and used without additional purification. For the adsorption experiments, stock solutions of dyes will be prepared by dissolving appropriate quantities of EBT in 1000 mL of distilled water. The working solutions will be freshly prepared by diluting stock solutions (1000 mg L^{-1}). The pH of solutions will be adjusted to the desired values by adding either 0.1 M HCl and/or NaOH.

Instrumentation

The dye concentration will be determined using UV spectrophotometer. The IR absorption bands will be taken by FTIR spectrometer in the wave range of 400-4000 cm^{-1}. The surface morphological structure will be observed using SEM technique. The pH of the dye solution will be measured in digital pH meter.

Preparation of activated cane sugar bagasse

The cane sugar bagasse will be obtained from sugar industries. It will be washed with distilled water, dried and powder in a mixer grinder. The dry sample will be sieved and then dried at 110^{o}C for 6 hours. Finally, it will be preserved in a desiccator.

Adsorption studies

The batch experiments will be carried out in 250 ml pyrex bottle with 100 mL of EBT dye solution containing 0.25g of activated cane sugar bagasse (ACSB), will be shaken in an orbit shaker at 250rpm to investigate the effects of contact time, initial dye concentration, temperature, pH, agitation speed and activation time on the adsorption process. Before and after adsorption of the EBT dye concentration will be measured by using UV spectrometer at wave length of 529nm. To calculate for the amount of EBT dye adsorbed on the ACSB and percentage of adsorption of EBT Eq.1 and 2 will be used respectively (Ahmed and Dhedan, 2012: Ahmedna, et al., 2000).

q_e = ... 1

and,

$$\%removal = \frac{C_i - C_e}{C_e} \times 100 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where qe is the adsorption capacity (mg/g) of ACSB at equilibrium, Ci and Ce are initial and equilibrium concentration of EBT (mg/L) respectively, V is the volume of EBT dye solution and M is the weight of ACSB.

Kinetic and thermodynamic study

In order to find out the adsorption rate of EBT dye solution by ACSB kinetic study will be carried out. Adsorption kinetic study will be carried out using 100 ml of EBT dye (8.5 mg/L) solution having 0.25g of ACSB at 34°C. It will be stirred in orbit shaker at 250rpm and concentration is measured at different time intervals (10-100min). Thermodynamic parameters will be calculated by executing the experiment at different temperature (30-40°C).

RESULTS AND DISCUSSION

SEM ANALYSIS

The surface morphology of the adsorbent material was taken before and after dye on cane sugar.

Fig 1(a) shows the surface texture, porosity and heterogeneous surface of the cane sugar, while fig 1(b) shows distinguished dark spots which exhibit clearly the dye loaded on the adsorbent surface.

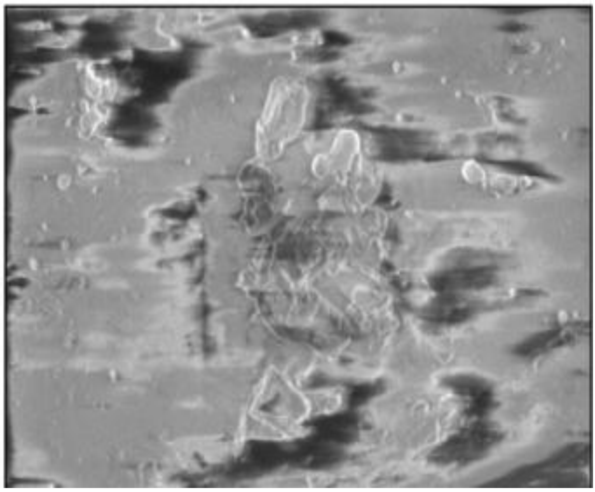


Figure 1 (a): SEM of cane sugar before adsorption

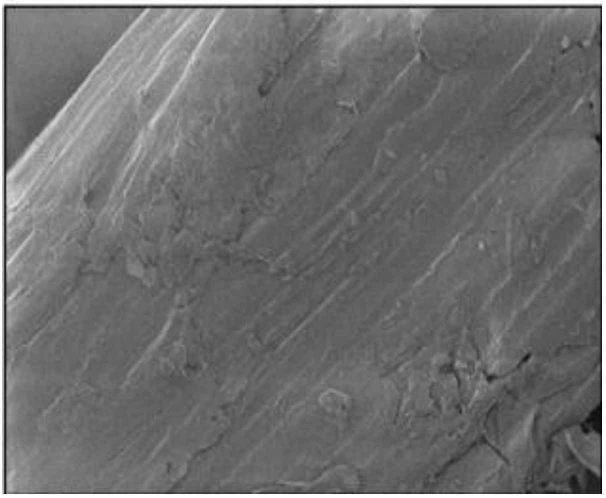


Figure 1 (b): SEM of cane sugar after adsorption

Fig 2a shows the FT-IR spectrum of the active cane sugar bagasse. The peak observed at 3403.03cm^{-1}, 2976.95cm^{-1} and 1571.29cm^{-1} denotes the presence of N-H stretching, C-H stretching and C=C aromatic. The peak which appeared at active cane sugar bagasse may be attributed to C-OH stretching (El Hendawy, 2006).

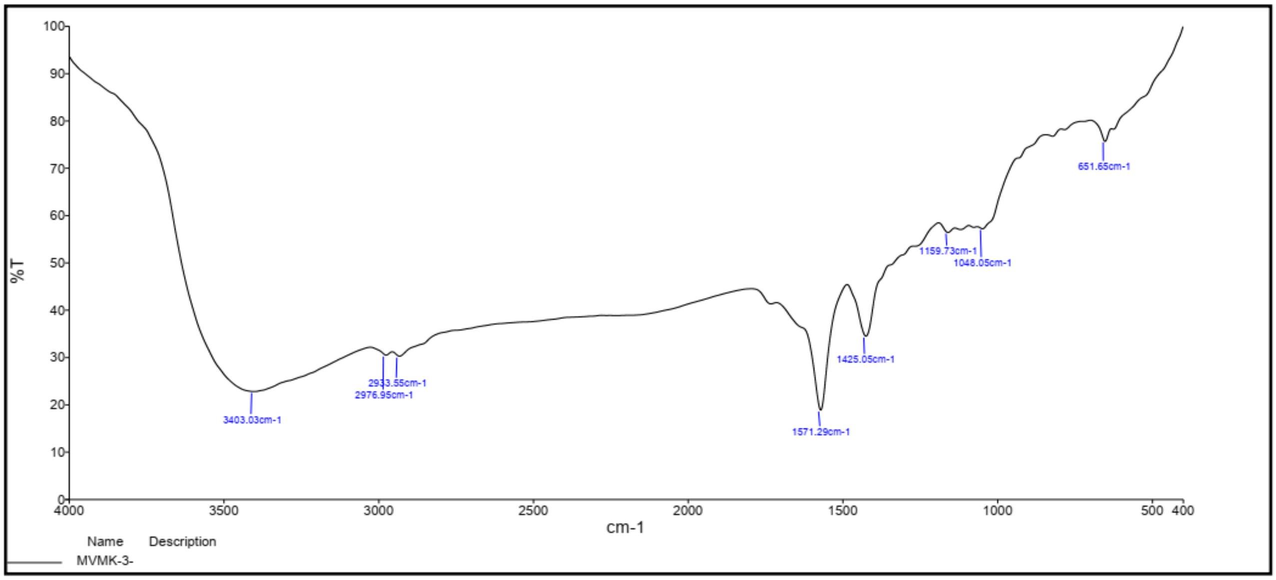


Figure 2 (a): FT-IR spectrum of cane sugar bagasse before adsorption

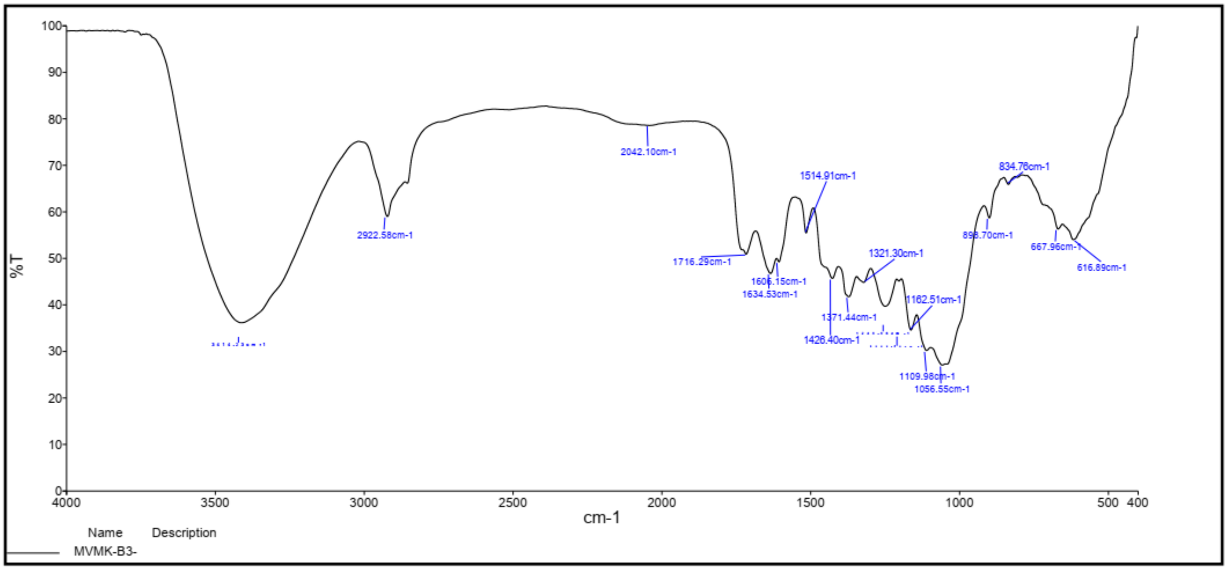


Figure 2 (b): FT-IR spectrum of cane sugar bagasse after adsorption

Figure 2b represents a typical FT-IR spectrum of dye adsorbed by cane sugar bagasse. It shows the appearance of a new peak at 1716.29cm^{-1} which is an indication for the presence of C=O ketone group at the surface of the cane sugar bagasse and it is due to the adsorption of the EBT dye from the aqueous solution.

ADSORPTION STUDIES

Variation of contact time

Batch experiment was performed at 34^{o}Cwith initial dye concentration of 8.5 mg/L using activated cane sugar bagasse dose at 2.5g/L at pH 7 with agitation speed of 250rpm in an orbit shaker. The equilibrium data shows that the variation of contact time from 10 to 100 minutes on EBT dye removed at 100 min. was considered as optimum time for maximum adsorption.

Variation of initial concentration

The effect if different initial dye concentrations is studied by (7.5-9.5 mg/L) maintaining the dose of activated cane sugar bagasse at 2.5g/L, contact time to 100min, temperature at 34^{o}C, pH 7 and agitation speed at 250rpm. The adsorption data depicts that the % decolourisation follows decreasing trend with increasing initial dye concentration. This may be due to the formation of monolayer of dyes on the surface of ACSB which hinders the further layers.

Variation of ACSB dosage

The effect of ACSB dose was carried out by varying the ACSB mass from 1.5 to 3.5g/L keeping contact time to 100min, dye concentration of 8.5mg/L, temperature at 34^{o}C, pH 7 and agitation speed at 250rpm. Fig 3(a) shows that the dye removal increased with increase in ACSB dosage due to increased amount of adsorption sites.

Variation of temperature

The effect temperature was studied by varying the different temperature (34, 37 and 40^{o}C) maintaining contact time to 100min, dye concentration to 8.5mg/L, ACSB dose 2.5g/L, pH 7 AND agitation speed at 250rpm. The equilibrium data evident that % decolourisation increased with increasing temperature due to the excitation of adsorbent particles.

Variation of pH

The effect of pH was studied by varying different pH (4, 7 and 9) keeping contact time to 100min, initial dye concentration 8.5mg/L, ACSB dose, 2.5g/L, temperature at 34^{o}C and agitation speed at 250rpm. Fig 3b shows that the adsorption of EBT increases with the decrease of pH of the solution. The initial pH may affect the charge on the adsorbent surface, altering its adsorption capacity (Annadurai, *et. al.*, 2002).

Variation of agitation speed

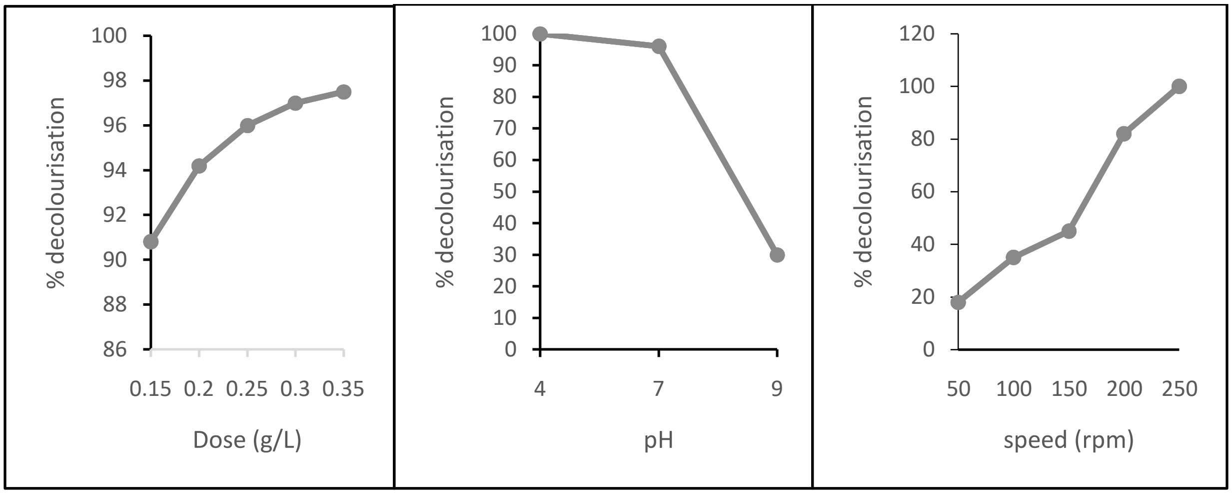
The effect of agitation speed of EBT on ACSB was studied by varying the agitation speed from 50 to 250rpm, keeping the other parameters at constant. It was observed that the adsorption of EBT is found to increase with increasing agitation speed due to the fact that with the increased turbulence, there is a decrease in boundary layer thickness around the adsorbent particles.

Variation of activation time

The effect of activation time of ACSB on the rate of adsorption was investigated by varying the time of activation (30min to 120min) and other parameters are constant. The adsorption data illustrated that the activation time increases the amount of dye adsorbed.

Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling the spent adsorbent and dye is essential (Zhao *et. al., 2015*). The desorption experiment was carried out with 0.1N NaOH. Fig 3c shows that the desorption efficiency increases with increase in strength of NaOH due to ion substitution.



(a) (b) (c)

Figure 3: Variation of ACSB dose (a), pH (b) and desorption (c)

ADSORPTION ISOTHERM STUDIES

The parameters obtained from different isotherm models provide information about adsorption mechanism and the surface properties of the adsorbent. Linear regression coefficient is frequently used to determine the best fitting isotherm.

Freundlich isotherm

This is an empirical relation between the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact. The expression below is the linear form of Freundlich equation.

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 3$$

where q_e is the amount of the dye adsorbed per unit mass of adsorbent (mg/g) at equilibrium, K_f and n are freundlich constants. The slope 1/n indicates the favorable adsorption with the attractive force between adsorbed species (Renugadevi, *et. al.*, 2010).

Langmuir isotherm

This is precise for the monolayer adsorption of a solute from a liquid on the adsorbent surface containing a definite number of identical active sites. The linear equation of Langmuir isotherm is expressed by:

$$C_e/q_e = 1/Q_o b + Ce/Q_o. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 4$$

Where Q_o and b are Langmuir constants.

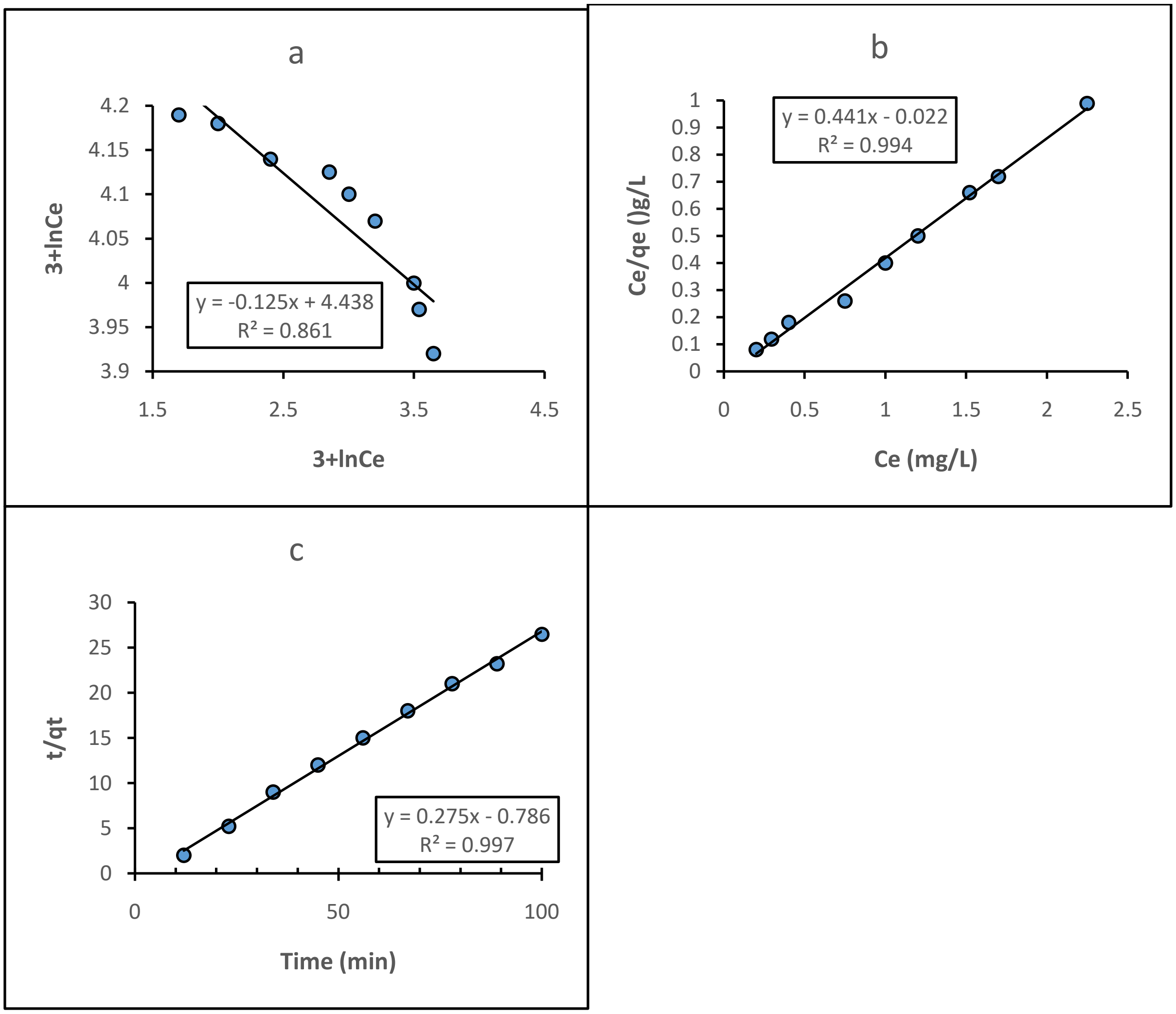


Figure 4: (a) Freundlich (b) Langmuir (c) Pseudo-second order kinetics

ADSORPTION KINETICS

The kinetics of the decolourisation of EBT dye solution was studied using pseudo-first and pseudo-second order kinetic models.

pseudo-first order kinetic models

Pseudo-first order model (Ho, *et. al.*, 2000) is given by:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad . \; . \quad 5$$

Where q_e and q_t are the adsorption capacity at equilibrium and at time t respectively, k_1 is the rate constant of the pseudo-first order equation.

After integration, the integrated form of the above equation becomes:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad 6$$

The equilibrium data shows that the adsorption of EBT onto ACSB cannot be applied and the reaction mechanism is not a first order reaction.

Pseudo-second order kinetics

Pseudo-second order kinetics (Ho, *et. al.*, 2000) can be expressed as:

$$\frac{dq_t}{d_t} = k_2(q_e - q_t)^2 \quad . \quad 7$$

Where k_2 is the rate constant of pseudo-second order adsorption.

After integration, the equation becomes:

$$\frac{t}{q_t} = \frac{1}{k_2} (q_e)^2 + \frac{t}{q_e} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad 8$$

The plot was a perfect linear which shows that the reaction kinetics follows pseudo-second order model. The correlation coefficients (R^2) also confirmed that the adsorption better fitted to pseudo-second order kinetics model than pseudo-first order kinetics.

THERMODYNAMICS STUDY

The Gibbs free energy change of the adsorption process (Kul and Koyuncu, 2010) is related to the equilibrium constant by the Van't Hoff equation.

$$\Delta G^o = -RT\ln K_L. \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad 9$$

Where kL (L/g) is an equilibrium constant obtained by multiplying the Langmuir constants $Q_o$and b, T is the absolute temperature (K), R is the gas constant. The graph was plotted by taking ΔG^o and T as y-axis and x-axis respectively. The relationship between the change in the gibbs free energy (ΔG^o), entropy (ΔS^o) and enthalpy (ΔH^o) can be expressed as follows:

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad 10$$

ΔS^o and ΔH^o can be calculated from the slope and intercept of the plot respectively. The negative value of ΔG^o (-4.8879) and positive value of ΔH^o (+0.5709) indicates that the process is spontaneous and feasible, it also indicates the endothermic nature of the adsorption. The positive value of ΔS^o (+0.0505) suggests that reflects of the affinity of adsorbent for dye.

Conclusion

In this study, ACSB was prepared by simple process and used for the adsorption of EBT from aqueous solution. Adsorption efficiency of ACSB for EBT at equilibrium time of 100min was found to be 97%. The parameters influencing adsorption rate, such as contact time, initial dye concentration, temperature, pH, etc. were optimized. The equilibrium results were analyzed using Freundlich and Langmuir adsorption isotherm models. The equilibrium data was best fitted to the Langmuir adsorption isotherm model than Freundlich adsorption isotherm model. The adsorption process was found to follow pseudo-second order kinetics. In the thermodynamics study, negative value of ΔG^o and positive value of ΔH^o indicate that the adsorption process is spontaneous, feasible and endothermic in nature. The positive value ΔS^o reflects the affinity of adsorbent dye. Thus, this study has proved that ACSB could be used as an efficient adsorbent for the removal of EBT dye from aqueous solution. Besides the use of ACSB as adsorbent to help with environmental pollution, it also helps reduce the cost of waste water treatment and reduce the amount of industrial byproducts.

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