APPLICATION OF POLYANILINE /SAWDUST COMPOSITE FOR REMOVAL OF ACID GREEN 25 FROM AQUEOUS SOLUTIONS: KINETICS AND THERMODYNAMIC STUDIES

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This research deals with the application of polyaniline coated onto wood sawdust (PAni/SD) for the removal of anionic or acidic dyes from aqueous solutions. Acid Green 25 (AG25) was selected as test probe throughout of the current investigation as a typical anionic dye. Adsorption experiments were carried out using batch system in order to do equilibrium adsorption isotherm, kinetics and thermodynamic studies. The results indicated that unmodified wood sawdust is a very poor adsorbent for anionic dyes, but when coated by polyaniline (PAni/SD), it is changed into a very efficient adsorbent material for adsorption of AG25 from aqueous solutions. It was found that chemical modification of agricultural wastes such as sawdust with polyaniline is leaded to a great enhancement in anionic dye removal efficiency. The findings seem to be important for application of the introduced biocomposite of polyaniline as an efficient new nonconventional adsorbent in dye removal technology.

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Introduction

To remove dyes and other colored contaminants from wastewaters, several physical, chemical, physico-chemical and biological such as coagulation and flocculation, membrane separation, different advance oxidation processes, ozonations, electro-coagulation, and adsorption.[1-5] Among these methods, adsorption currently appears to offer the best potential for overall treatment methods have been developed.[6] Therefore, in recent years, considerable attention has been devoted to the study of different types of low-cost inorganics, biomaterials and agricultural wastes or byproducts for removal of dyes or other toxic materials such as heavy metals from aqueous solutions.[7-15] In any adsorption process, the interactions between adsorbent and adsorbates arises from different intermolecular interactions such as Van der Waals forces, hydrophobic forces, H-bonding, ion exchange, dipole-dipole interactions and chemical bonds. However, it has been well established that the biomaterials by themselves or without modification have limited sorption performance. So, in order to enhance their sorption capacity, there is a need to do a suitable chemical modification. The first step in interpreting the adsorption data for describing the performance of a given adsorbent or comparing the performance of two or more adsorbents is to plot an adsorption isotherm that will describe the equilibrium distribution of solute between the solid and liquid phases.

In the present paper sawdust was employed as a very cheap and environmentally friendly substrate for chemical modification (coating) before adsorption experiments. Polyaniline (PAni) was employed for coating or modification of sawdust. Based on our previous study, it has been found that conducting polymers such as polypyrrole, polyaniline and polythiophene can efficiently improve the sorption capacity of sawdust toward various dyes.[16-19] The effects of different system variables such as adsorbent dose, initial dye concentration, pH of test solution, temperature, and contact time have already been studied and the optimized conditions obtained were used for the current isotherm, kinetics and thermodynamic studies.[18] The current investigation is mainly focused on isotherm, kinetics and thermodynamic studies carried out on the modified sawdust by polyaniline (PAni/SD). Due to the nature of the various reactive functional groups in agricultural wastes (e.g. chelating or ion exchange properties), they are mostly useful for uptake of cationic species such as heavy metal ions or cationic dyes from aqueous solutions.[16] On the other hand unmodified or raw sawdust is a very poor sorbent for removal of anionic dyes. So, the aim of this work is to improve sorption characteristics of sawdust via chemical modification using polyaniline. Sawdust was found a proper choice because it is available as plentiful and almost free of charge. It was also found a suitable substrate for sorption of aniline in acidic media and then for subsequent in-situ polymerization for preparing a novel biocomposite adsorbent for dye removal.

Experimental

Materials and methods

All the chemicals were used were analytical reagents grade and were prepared in distilled water. Sawdust samples (SD) prepared from Narra wood was obtained from a local carpentry workshop. Aniline was obtained from Merck and distilled before use. A single beam Perkin-Elmer UV–Vis spectrophotometer with a 1 cm cell was used for measuring all of absorption data. A Metrohm pH meter (Model 827) with a combined double junction glass electrode was used for pH measurements. pH adjustments were carried out using dilute NaOH and HCl solutions. Acid green dye termed as AG25 (chemical formula=$C_{28}H_{20}N_2Na_2O_8S_2$, MW= 622.58 g mol^{-1}) was employed as a typical anionic

acidic dye for the current investigation (Fig. 1). An accurately weighed quantity (1.0 g) of AG25 was dissolved in double distilled water to prepare stock solution of 100 mg L^{-1}. Experimental solutions of the desired concentrations were prepared by dilution of stock solution with double-distilled water.

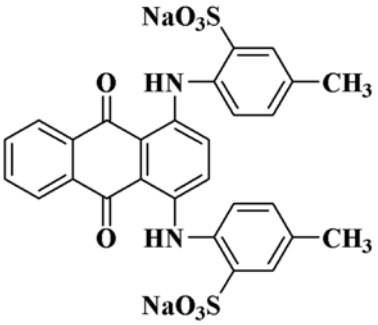

Figure 1. Chemical structure of AG25 dye.

The analysis of test dye solutions for AG25 was carried out spectrophotometry using a UV-vis spectrophotometer at a wavelength corresponding to the maximum absorbance of the dye (λ_{max}=642 nm). Calibration curve was plotted based on absorbance versus concentration of the dye solution at maximum wavelength of the dye using Beer's law ($A=\varepsilon bc$).

Preparation of polyaniline coated sawdust (PAni/SD)

In order to prepare polymer coated onto sawdust (termed as PAni/SD), 10.0 g sawdust (35-50 mesh) immersed in 100 mL of 0.20 M freshly distilled aniline solution for 12 h before polymerization.[18] The excess of the monomer solution was removed by simple decantation. 50 mL of oxidant solution [(0.20 M) $(NH_4)_2S_2O_8$)] was added into the mixture gradually, and the reaction was allowed to continue for 5 h at room temperature. Polymer coated sawdust (PAni/SD) was filtered, washed with sufficient distilled water, and then was dried in an oven at temperature about 60 ^oC before use.

Adsorption experiments

Batch equilibrium studies were carried out by adding a fixed amount of the sorbent into 250 mL Erlenmeyer flasks containing 50.0 mL of different initial concentrations (20-100 mg L^{-1}) of dye solution at the optimised pH value that has previously been found to be about 2.0. [18] The flasks were agitated in a mechanical shaker at 100 rpm at room temperature for 60 min. At the end of pre-determined time intervals, adsorbent was removed by simple filtration. The filtrates were analyzed for the residual (unadsorbed) concentration of AG25 dye. The following equations were used to calculate the percentage of sorption (φ) and the amount of adsorbed AG25, respectively:

$$\varphi=\frac{(C_o-C_e)}{C_o}\times 100 \qquad (1)$$

$$\frac{x}{m_1}=\frac{(C_o-C_e)V_1}{m_1} \qquad (2)$$

where

C_o and C_e are the respective initial (inlet) and equilibrium (outlet) concentrations (mg L^{-1}) of AG25;

X/m_1 is the amount of AG25 adsorbed onto unit amount of the adsorbent (mg g^{-1}) at equilibrium;

V_1 is the volume of the test solution used in the adsorption experiment (L).

Alternatively, regeneration of the used adsorbent was also examined (Eqs. 3, 4).

$$\xi=\frac{m_2}{m_o}\times 100 \qquad (3)$$

$$m_o=(C_o-C_e)V_2 \qquad (4a)$$

$$m_2=C_eV_2 \qquad (4b)$$

where,

ξ is the desorption, in %,

m_0 is the initially adsorbed AG25 dye (mg) onto adsorbent

m_2 is the released dye or the concentration of AG25 in the regenerated solution (mg)

V_2 is the volume (L) of the eluent or washing solution.

Adsorption isotherm

In this study in order to facilitate estimation of the adsorption capacities the two well-known equilibrium adsorption models, Freundlich and Langmuir, were employed for the treatments of the equilibrium adsorption data.[20,21] The Langmuir isotherm is a semi-empirical isotherm derived from a proposed kinetic mechanism. Langmuir assumed that a surface consists of a given number of equivalent sites where a species can stick on the surface of a solid adsorbent through van der Waals' interactions (called physisorption) or through the formation of covalent bonds (called chemisorptions). The Langmuir model is represented by Eq. (5):

$$q_e=\frac{Q_0bC_e}{1+bC_e} \qquad (5)$$

Eq. (5) can be rearranged to linear form:

$$\frac{C_e}{q_e}=\frac{1}{Q_0b}+\left(\frac{1}{Q_0}\right)C_e \qquad (6)$$

where,

q_e is the amount sorbate adsorbed per unit mass of adsorbent (mg g^{-1}),

Q_o is the maximum amount sorbed (mg g^{-1}) when the monolayer is complete,

b is Langmuir's constant related to the affinity of binding sites and is a measure of the energy or enthalpy of adsorption (L mg^{-1}).

The magnitude of b quantifies the relative affinity that a given solute has for surface adsorption. Like all equilibrium constants, *b* is temperature dependent. A linearized plot of Ce/q_e against C_e gives Q_o and *b* values. Values of Q_o and b were calculated from the slopes ($1/Q_o$) and intercept ($1/bQ_o$) of the linear plots. Another widely used equation in adsorption processes is the Freundlich equation. The Freundlich isotherm is the earliest known relationship describing the sorption equation. This fairly satisfactory empirical isotherm can be used for non-ideal sorption that involves heterogeneous sorption and is expressed by the following equation:

$$q_e = \frac{x}{m} = k_f C_e^{1/n} \quad (7)$$

Eq. (7) can be rearranged to linear form:

$$\lg \frac{x}{m} = \lg k_f + \frac{1}{n} \lg C_e \quad (8)$$

where,

x/m is the equilibrium adsorption capacity (mg g^{-1}),

C_e is the equilibrium or residual concentration (mg L^{-1}) of AG25 dye in solution, K and *n* are empirical constants for each adsorbent-adsorbate pair at a given temperature indicating sorption capacity of adsorbent and intensity of adsorption [(mg g^{-1} (g $L^{-1})^n$], respectively.

$1/n$ is the heterogeneity factor and a relatively slight slope and hence a small value of $1/n$ <1 indicates that, the sorption system is favourable and good over entire range of concentration investigated. While values close to or even 1.0 indicate materials with relatively homogenous binding sites. A high value of K_f also indicates a high adsorption capacity of an adsorbent. The adsorption isotherms using both Langmuir and Freundlich equations (linear forms) obtained for removal of AG25 have been depicted in Figs. 2 and 3 respectively.

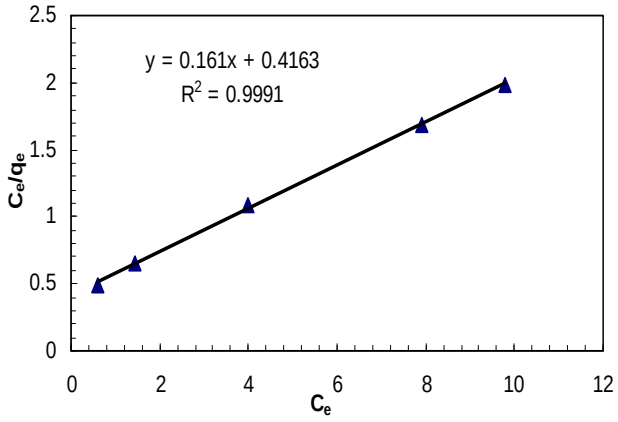

Figure 2. Langmuir isotherms for the sorption of AG25 by PAni/SD.

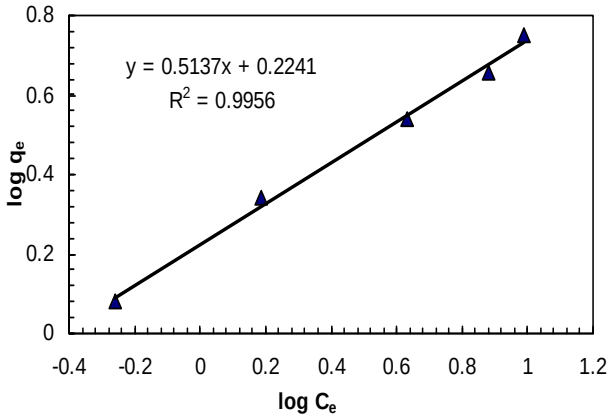

Figure 3. Freundlich adsorption isotherms for the sorption of AG25 by PAni/SD. (Conditions: amount of adsorbent= 0.80 g, C_o = 20-100 mg L^{-1}, time = 60 min, pH=2).

The Langmuir and Freundlich isotherm constants obtained from the related linear equations are summarized in Table 1. The correlation coefficients (R^2) indicate that both Langmuir and Freundlich equations were satisfactory, but the Langmuir isotherm fits the equilibrium data better which confirms chemisorption mechanism during dye removal. The value of n confirms that the adsorption system is suitable. For a suitable adsorption system the value of n is usually between 1 and 10 which implies that the surface of adsorbent is heterogeneous in nature. All the experiments were carried out in triplicate at each condition whose mean values with maximum RSD was less than 1% are presented.

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation, the type of isotherm and is defined by the following equation:

$$R_L = \frac{1}{1+bC_0} \quad (9)$$

where,

b (L mg^{-1}) is the Langmuir constant and C_o is the initial dye concentration (mg L^{-1}). The value of R_L indicates the shape of the isotherms to be either unfavorable (R_L> 1), linear (R_L=1), favorable (0< R_L<1) or irreversible (R_L=0).[22] As observed, R_L factor value is changing from 0.025 to 0.11 for different dye concentrations of 20–100 (mg L^{-1}) that indicates favourable adsorption, since it is lying between 0 and 1.

Adsorption kinetics

A study of kinetics of adsorption is desirable as it provides information about the mechanism of adsorption, which is important for efficiency of the process. The kinetic data of adsorption can be evaluated using different types of mathematical models, of which the one most widely used is the Lagergren's rate equation.[23] The kinetics of the adsorption process was analyzed using the pseudo-first-order rate equation as given below (Eq.10):

$$\lg(q_e - q_t) = \lg(q_e) - \frac{K_1 t}{2.303} \quad (10)$$

Table 1. Freundlich and Longmuir isotherms constants for adsorption of AG25 onto PAni/SD

	Freundlich isotherm parameters			Langmuir isotherm parameters		
Adsorbent	K_F (mg g^{-1})(g L^{-1})^n	n	R^2	Q_o (mg g^{-1})	b (L mg^{-1})	R^2
PAni/SD	1.67	1.95	0.9952	6.21	0.38	0.9991

where,

q_t and q_e (mg g^{-1}) are the amounts of dye adsorbed per unit mass of the adsorbent at time t and at equilibrium, respectively.

k_1 (min^{-1}) is the pseudo-first-order rate constant of adsorption.

As the Eq. (10) shows, there is a linear relationship between lg (q_e-q_t) and t. The slope of the plot lg (q_e-q_t) versus t gives the value of K_1 and the value of q_e can be calculated from intercept (Fig.4).

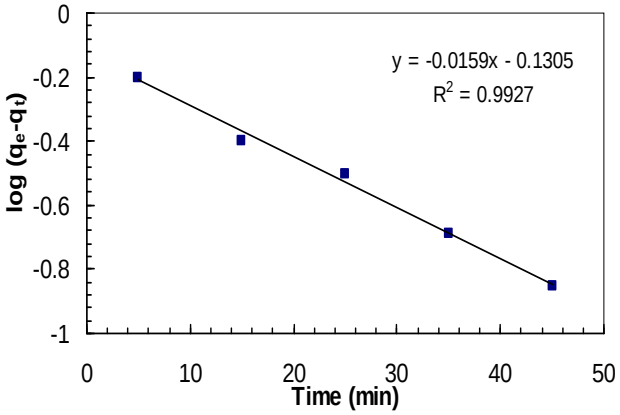

Fig. 4. The pseudo-first-order kinetics for the sorption of AG25 by PAni/SD. (Conditions: m =0.80 g, C_o = 50 mg L^{-1}, pH= 2).

Kinetic data were further applied to the pseudo-second-order kinetic model proposed by Ho and McKay.[24] The differential equation has the following form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right)t \qquad (11)$$

where,

K_2 is the second order rate constant (g mg^{-1} min^{-1}).

The plot of t/q_t versus t should give straight lines where slopes and intercepts are respectively $1/q_e$ and $1/K_2 q_e^2$ (Fig.5). The values of the rate constant K_2 and of the equilibrium sorption capacity q_e are calculated from these parameters. The values of rate constants and correlation coefficients for these kinetic models are also shown in Table 2.

As the correlation coefficients calculated for the second order kinetic model (R^2=0.998) and also the good agreement of calculated $q_{e2,calc.}$ (3.04) and experimental $q_{e,exp.}$ (2.95) values indicate, the adsorption system follows the pseudo second order kinetic model and a chemisorption mechanism is therefore suggested.

Table 2. Kinetic parameters for the adsorption of AG25 by PAni/SD

First-order kinetic model				Second-order kinetic model			
$q_{e,exp}$ mg g^{-1}	K_1 min^{-1}	$q_{e1,calc.}$ mg g^{-1}	R^2	K_2 g mg^{-1}min^{-1}	$q_{e2,calc.}$ mg g^{-1}	R^2	
2.95	0.037	0.74	0.9927	0.12	3.04	0.9981	

Adsorption thermodynamics

In understanding better the effect of temperature on the adsorption, it is important to study the thermodynamic parameters such as standard Gibbs free energy change, standard enthalpy, and standard entropy. The Gibbs free energy of adsorption by using equilibrium constant (K_c) is calculated from the following equation.[25]

$$\Delta G^{o} = -RT \ln K_C \qquad (13)$$

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} \qquad (14)$$

Standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0), of adsorption can be estimated from van't Hoff equation given in:

$$\ln K_C = \frac{-\Delta H^{o}_{ads}}{RT} + \frac{\Delta S^{o}}{R} \qquad (15)$$

where,

T is absolute temperature

R is the gas constant (8.314 J mol^{-1} K^{-1}),

K_c is adsorption equilibrium constant.

The K_c value is calculated from the Eq. (16):

$$K_C = \frac{C_{Ae}}{C_{Se}} \qquad (16)$$

where

C_{Ae} is the amount of dye adsorbed on the adsorbent per liter of the solution at equilibrium (mg L^{-1}); C_{Se} is the equilibrium concentration of the dye in the solution (mg L^{-1}). The plot of lnK_c against $1/T$ (K^{-1}) should be linear.

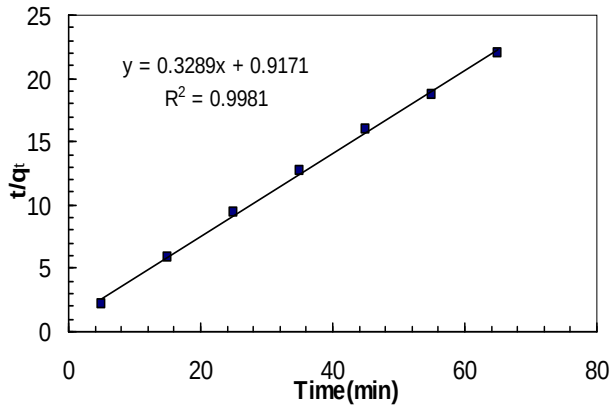

Figure 5. The pseudo-second-order kinetics for the sorption of AG25 by PAni/SD. (Conditions: m =1.0 g, C_o = 50 mg L^{-1}, pH= 2).

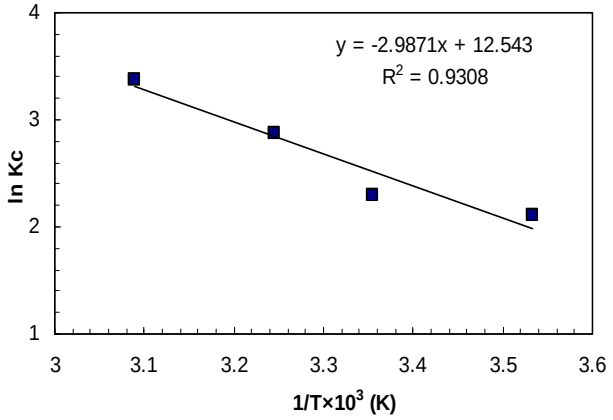

Figure 6. Plot of ln k_c against reciprocal temperature for the adsorption of AG25 by PAni/SD. (Conditions: m=0.80 g, C_o=50.0 mg L^{-1}, t = 60 min, pH=2).

The slope of the van't Hoff plot is equal to, and its intercept is equal to. The van't Hoff plot for the adsorption of AG25 onto PAni/SD is given in Fig. 6.

Thermodynamic parameters obtained are given in Table 3. As shown in the table 3, the negative values of ΔG^o at different temperatures indicate the spontaneous nature of the adsorption process. The decrease in $\Delta G°$ with rise in temperature indicate that better sorption of dye is obtained at a higher temperature. The positive value of $\Delta S°$ also indicates the increased randomness during the uptake of AG25 dye onto PAni/SD particles and reflects the affinity of the PAni/SD for AG25 dye. With displacement of the adsorbed water molecules by the dye molecules, more translational entropy is gained, thus allowing the prevalence of randomness in the system. Positive value of ΔH^o reveals endothermic nature of adsorption and it governs the possibility of physical adsorption. In physisorption ((ΔH~5 cal mol^{-1}) electrostatic attractions are the basic physical forces in most adsorption reactions (e.g. dipole-dipole, dispersion, London-van der Waals and H-bonding). Chemisorptions (ΔH=10-100 kcal mol^{-1}) involve the formation of strong chemical bonds between adsorbates and specific surface locations known as chemically active sites.

Table 3. Thermodynamic parameters for the adsorption of AG25 by PAni/SD

T, K	K_c	ΔG^o, kJ	ΔH^o, kJ	ΔS^o, J K^{-1}
283	8.3	-4.8	+24.8	+104.3
298	9.3	-5.5		
308	18.0	-7.4		
328	29.4	-9.1		

The entropy change (ΔS^0=104.3 J/K) means that adsorption or removal of anionic dye of AG25 onto PAni/SD corresponds to a increase in entropy and suggests the increased randomness at the solid/liquid interface during adsorption. Hydrophobic interactions are hypothesized to result in greater overall system entropy. So, hydrophobic interactions played a dominant role in the adsorption of AG25 by PAni/SD.

Conclusions

PAni/SD can be simply prepared via direct chemical synthesis of aniline monomer on the surface of biomaterial wastes. The polyaniline/sawdust composite can be efficiently employed for anionic dye removal under acidic conditions. Among the parameters investigated, pH of dye solution has a profound effect on dye uptake by both treated and unmodified sawdust. Both adsorbents are more effective for anionic dye removal under acidic conditions. From the kinetic and thermodynamic investigations, it was found that the AG25 dye removal by PAni/SD is occurred mostly via chemisorption process and the adsorption is spontaneous. Since the enthalpy change is positive, so it could be concluded that the sorption process is endothermic. Positive value of entropy indicates that the entropy and the hydrophobic forces are the driving force for AG25 dye removal by the introduced adsorbent.

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