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Thermo-Kinetics Studies of Dye Removal with Kaolin from *Tectona grandis* and Indigo Dye Effluents

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Abstract. The kinetics and thermodynamic behaviour of dye molecules removed from *Tectona grandis* and indigo dye effluents using kaolin as the coagulant were studied and the results obtained were compared with the commercial alum (as standard). Comparison of data obtained from Langmuir and Freundlich isotherms indicated that the coagulation process was chemisorptions. The isotherm parameters of Langmuir isotherm such as coagulation capacity Q_o; coagulation energy intensity b; and correlation coefficient R^2, in this study were greater than that of Freundlich. The correlation coefficient of the pseudo-second-order kinetics was almost equal to unity and the values of $q_{e(Cal.)}$ were of insignificant difference from the corresponding $q_{e(exp.)}$ and these made the pseudo-second-order kinetics fitted well with the coagulation process. The thermodynamic parameters (ΔH and ΔS) obtained indicated that the coagulation process was endothermic and spontaneous, respectively. The negative values of ΔG shows the irreversible nature of the coagulation process and the correlation coefficients (R^2) closed to unity indicates the fitness of the coagulation thermodynamics with the experimental data.

Keywords. coagulant, effluents, kinetics, endothermic, thermodynamics

Introduction

Waste water generated at various stages in textile industry differ in composition, strength and volume. When not properly treated before discharged into rivers, it pollutes the receiving water body by causing injury to the aquatic plants, animals and making the water unfit for human consumption (Dae-Hee *et al.,* 1999).

According to Chakrabarti *et al.* (1988) most of the available dyes and pigments consisting of over 7,000 different chemical structures used in textile industry are completely resistant to biodegradation processes and for this reason, physical process for their removal from the effluent is recommended. Chemical process may increase the harmful effect of the effluent on the receiving water body (Pitter and Chudoba, 1990). The conventional physical methods of treating effluent are sorption with the aid of chitin called ozonization method (Safarik, 1995), organic carbon (Murphy *et al.,* 1992; Gupta *et al.,* 1990), and electrochemical oxidation (Lin and Peng, 1994). The high cost of the above mentioned methods led researchers to look for cost effective method (called coagulation) with equal or more removal efficiency than the conventional treatment methods.

Coagulation method has been found easy to operate and energy saving treatment alternatives (Hassani *et al.,* 2008). It can be expressed as the conversion of colloidal and dispersal particles into small visible floc upon addition of a simple coagulant. It brings about compression of the electrical double layer surrounding each suspended particle, as a result of decrease in the magnitude of the repulsive interactions between particles and destabilization of the particles. The most common coagulants used in wastewater treatment are alum $Al_2(SO_4)_3.12H_2O$, poly aluminium chloride (PAC) and sometimes kaolin. Poly aluminium chloride is more effective than alum in wastewater treatment but highly expensive and more toxic than alum with demerit of skin infection (like eczema) on consumer of the treated wastewater. As a result of these, kaolin is mostly preferred due to its abundance, environmental friendly and availability at low cost (Ma and Wang, 2006; Exall and Vanloon, 2003).

Kaolin has been reported by Ma and Wang (2006) to be used in treatment of oil polluted water with about 99 % removal of chemical oxygen demand, biological oxygen demand, total dissolve solids and hardness. Other areas where it is utilized are pharmaceutical industry, for production of drug used in treatment of various gastrointestinal problems; cosmetics for

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production of talc; production of glossy paper for magazine and newspaper; paints production for gloss level control, and insecticides to control arthropods (Barker *et al.,* 2007; Belloto *et al.,* 1995). The active chemical component responsible for wastewater treatment in kaolin is aluminium silicate hydroxide ($Al_2Si_2O_5(OH)_4$) popularly called kaolinite. It is a fine, white layered silicate mineral with one tetrahedral sheet linked through oxygen atom to one octahedral sheet of alumina octahedral (Deer *et al.,* 1992).

Thus, this research was primarily designed to focus on the kinetic and thermodynamic studies of the coagulation of *T. grandis* and indigo dyes' effluents using kaolin as coagulant.

Materials and Methods

The tender leaves of teak plant (*Tectona grandis)* and kaolin ($Al_2Si_2O_5(OH)_4$) were obtained from forestry plantation and Industrial Design Department of Federal University of Technology, Akure, Nigeria, respectively. Alum ($Al_2(SO_4)_3.12H_2O$) was purchased from Pasca Chemicals Store, Akure, Nigeria. Indigo dye and pre-bleached white cotton fabric were purchased from a dyestuff market in Akure, Nigeria. All the chemicals and equipment used were of analytical grade and obtained from Chemistry Department of Federal University of Technology, Akure, Nigeria.

Coagulation process. The effluents used in this study were procured from pilot dyeing of cellulosic fabric with indigo and the extracted *T. grandis* dye. These dye effluents then were subjected to coagulation/ flocculation process via jar experiment.

The effect of coagulant dosage, contact time and temperature on colour removal was studied by coagulation of *T. grandis* and indigo dye effluent with kaolin. The coagulant dosage was varied from 0.2 to 1.0 g with contact time 1.5 h, temperature of 303 K and agitation speed of 100 rpm using Gallenkamp orbital shaker. At the end of the contact time, the solutions were centrifuged at 500 rpm for 1.00 h using uniscope centrifuge machine and the absorbance of the supernatants read at 530 nm and 410 nm were used to extrapolate concentrations of the treated *T. grandis* and indigo dye effluent, respectively from prepared working curve using camspec spectrophotometer.

The effect of contact time on dye removal from the effluent was carried out by varying contact time from 0.5-3.5 h with coagulant dosages of 0.5 g, temperature of 303 K and agitation speed of 100 rpm. At the end of each pre-determined contact time, the solutions were treated as done in effect of coagulant dosage to obtain correspond concentration of dye removed from the effluent.

The effect of temperature on dye removal efficiency of the coagulant from generated dyeing effluents was studied by batch technique using Roaches dyeing machine. The coagulation temperature was varied from 303 K - 343 K with coagulant dosage of 0.5 g, contact time of 1.5 h and agitation speed of 100 rpm. The dyeing cups were removed from the dyeing machine at the end of 1.5 h contact time and the solutions therein were treated as done for previous removal technique to obtain percentage dye removal from the treated effluents (Rakhi and Vankar, 2007; Manaskorn *et al.,* 2004).

The data obtained from effect of coagulant dosage, contact time and temperature were used to obtain useful information for the isotherm, kinetics and thermo-dynamics studies.

Coagulation isotherm. Data obtained from effect of coagulant dosage were used for Langmuir and Freundlich isotherm studies using linearized equations $1/q_e = Q_o + 1/bQ_oC_e$ and $\log q_e = \log K_f + 1/n \log C_e$, respectively.

Where, q_e = amount of dye coagulated per unit weight of coagulant (mg/g), C_e = equilibrium concentration of the coagulant (mg/L), Q_o = Langmuir maximum monolayer coagulation capacity (or total number of binding sites) (mg/g), b = coagulation energy (L /mg), K_f and n are Freundlich constants, associated with coagulation capacity and intensity respectively (Himanshu and Vashi, 2010).

Coagulation kinetics. The data obtained from kinetic parameters for the coagulation process were analyzed with Lagergren pseudo-first-order and pseudo-second-order kinetic models expressed by the equations:

$$\text{Log}(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303}$$ (Lagergren pseudo-first-order linearized equation)

$$t/q_t = 1/K_2q^2_e + t/q_e$$ (Lagergren pseudo-second-order linearized equation)

Where, q_e and q_t refer to the quantity of dye coagulated (mg/g) at equilibrium and at any time, t (h), respectively, K_1 is the equilibrium rate constant of pseudo-first-order coagulation kinetic (h^{-1}) and K_2 is equilibrium rate constant of pseudo-second-order coagulation (g/mg h) (Adetuyi and Jabar, 2011).

Coagulation thermodynamics. Model of coagulation thermodynamic was investigated by using second law of thermodynamic equations expressed as:

$$\Delta G = \Delta H - T\Delta S$$
$$\Delta G = - RT \ln K_\theta$$

Equating the above equations, gave Van't Hoff equation below:

$$\text{Log } K_\theta = \frac{-\Delta H^\theta}{2.303\ RT} + \frac{\Delta S^\theta}{2.303\ R}$$

Where, K = thermodynamic equilibrium constant (C_{solid}/C_{liquid}), C_{solid} = solid phase dye concentration at equilibrium (mg/ L), C_{liquid} = liquid phase dye concentration at equilibrium (mg/ L), T = temperature in Kelvin, R = universal gas constant (8.314J/molK), ΔH^θ = standard enthalpy change (KJ/Mol), ΔS^θ = standard entropy change (KJ/Molk) and ΔG = free energy change (KJ/Mol) (Chan-Li *et al.,* 2007; Atkins and de Paula, 2006).

Results and Discussion

The calibration curves of *T. grandis* and indigo dye were prepared at wavelength of maximum absorption (λ_{max}) 530 nm and 410 nm, corresponding to the absorption of reddish-brown and greenish-yellow (leuco-dye), respectively (Adetuyi and Jabar, 2011; Adetuyi *et al.,* 2002). They were reproducible and linear over the calibration range used in this study.

Dye removal efficiency. The quantity of dye removed increased from 90.47 to 99.36 % as coagulant dosage increased from 0.2 g to 1 g in *T. grandis* while that of effluent from indigo dye was increased from 89.97 to 99.23 % using kaolin as coagulant, as against treatment using alum as standard coagulant with percentage removal of 88.98 to 98.73 % of *T. grandis* dye from the effluent and 88.43 % to 98.72 % indigo dye was removed from the effluent as coagulant dosage increased from 0.2 g to 1 g (Table 1). The data in this Table shows that kaolin has higher dye/ colour removal efficiency than the standard (alum). Hence, kaolin could be a good substitute of alum in industrial effluent treatment because it is cheaper and abundant.

Increase in contact time and temperature of coagulation process increased the percentage of colour removal in the effluents (Table 1-2). It was equally noticed that kaolin performed better than the chosen standard and it was more effective in treatment of *T. grandis* effluent than that of indigo.

Coagulation isotherm. ***Langmuir isotherm.*** Linearized Langmuir equation $1/q_e = Q_o + 1/bQ_oC_e$ was used to obtain isotherm data by plotting a graph of $1/q_e$ against $1/C_e$ as shown in Fig. 1, where intercept of the graph equal to Langmuir maximum monolayer coagulation capacity, Q_o and Langmuir constant b, called energy of coagulation process was gotten from the slope of the

Table 1. Effect of coagulant dosage and temperature on *Tectona grandis* and indigo dye effluents

Coagulant	Coagulant dosage (g)					Temperature (K)				
	0.2	0.4	0.6	0.8	1.0	303	313	323	333	343
	(colour removed %)					(colour removed %)				
KT	90.47	92.16	95.98	98.73	99.36	93.43	95.13	97.25	98.73	99.15
AT	88.98	91.10	95.76	98.09	98.73	92.37	93.43	95.76	98.09	98.52
KI	89.97	92.03	96.40	98.72	99.23	92.55	93.83	97.17	98.72	98.97
AI	88.43	91.52	95.89	98.20	98.72	92.03	93.57	96.14	98.20	98.46

Table 2. Effect of contact time on *Tectona grandis* and indigo dye effluents

Coagulant	Time (h)						
	0.50	1.00	1.50	2.00	2.50	3.00	3.50
	Colour removed (%)						
KT	91.53	94.28	96.40	97.67	98.73	98.94	98.94
AT	90.25	93.01	95.55	97.55	97.88	98.31	98.52
KI	90.23	91.77	95.37	96.92	98.20	98.46	98.46
AI	89.20	90.23	95.37	96.92	98.20	98.46	98.46

KT = Kaolin treated *T. grandis* dye effluent; AT = Alum treated *T. grandis* dye effluent; KI = Kaolin treated indigo dye effluent; AI = Alum treated indigo dye effluent.

graph and it was used to calculate Langmuir dimensionless separation factor, r. Table 3 shows intercept, slope and Langmuir constants for coagulation of *T. grandis* and indigo dyes, the maximum monolayer coagulation capacity Q_o of the coagulation for dye from the effluents, dimensionless factor r and correlation coefficient R^2 were found to be in order AT > KT and AI > KI. In contrary, the values of Langmuir constant b were found to be in order KT > AT and KI > AI, while the values of r < 1 show that the coagulation process is favourable.

Freundlich isotherm. Figure 2 shows graph of log q_e against log C_e from which, the slope and intercept are obtained (Table 3) and used to determine the adsorption capacity and intensity of coagulation process, respectively. Adsorption capacity K_f was in order KT > KI and AT > AI and adsorption intensity was in order KT > KI and AT = AI. Table 3 equally shows that kaolin has greater coagulation capacity and intensity than alum (standard), this observation further support the possibility of kaolin replacing alum for coagulation/ treatment of waste water. The values of coagulation intensity n > 1 in all treated effluent, is an indication of good coagulation process.

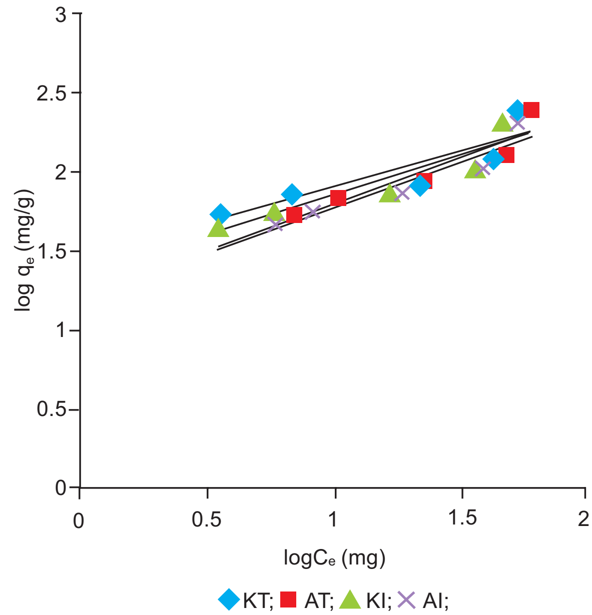

Fig. 2. Linearized Freundlich isotherm for *T. grandis* and indigo dye.

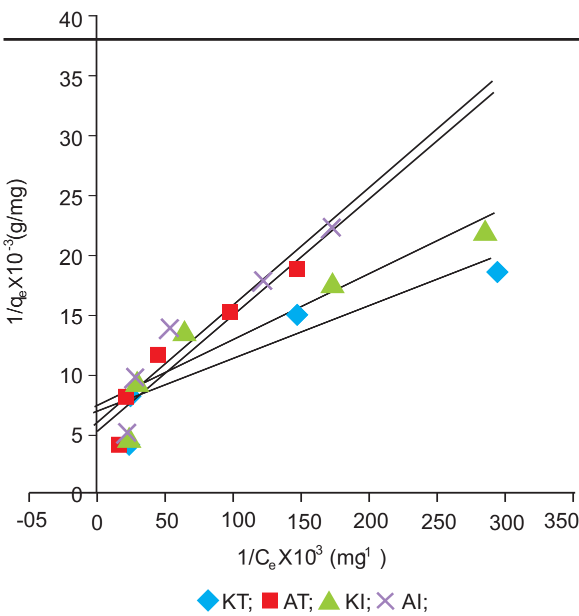

Fig. 1. Linearized Langmuir isotherm of *T.grandis* and indigo dye.

Comparison of data obtained from Langmuir and Freundlich isotherm indicated that the coagulation process was chemisorption since Langmuir coagulation capacities Q_o was greater than that of Freundlich K_f, Langmuir coagulation energy/ intensity b and correlation coefficient R^2 were also greater than that of Freundlich.

Coagulation kinetics. The data obtained from the plot in Fig. 3 (Lagergren first-order-kinetic) did not fit well

Table 3. Coagulation isotherm and thermodynamics parameters for *Tectona grandis* and indigo dye effluents

	Langmuir						Freundlich					Thermodynamics (Van't Hoff)					
Coag.	$C \times 10^{-3}$ (mg/g)	Slope (g)	Q_O (mg/g)	b (L/mg)	r	R^2	C (mg/g)	Slope (g^{-1})	k_f (mg/g)	n (g^{-1})	R^2	C	Slope (K)	ΔH(KJ/ Mol)	ΔS(KJ/ MolK)	ΔG(KJ/ Mol)	R^2
KT	6.78	0.04	147.56	0.15	0.01	0.81	1.44	0.46	27.67	2.19	0.81	9.41	- 2.52	48.27	0.18	- 6.33	0.98
AT	5.18	0.10	193.13	0.05	0.03	0.90	1.21	0.59	16.18	1.71	0.87	7.97	- 2.11	40.40	0.15	- 5.8	0.94
KI	7.28	0.06	137.40	0.13	0.02	0.87	1.36	0.49	22.75	2.04	0.85	9.54	- 2.58	49.30	0.18	- 5.95	0.96
AI	6.00	0.10	167.25	0.06	0.04	0.91	1.18	0.59	15.24	1.71	0.90	8.07	- 2.14	40.96	0.15	- 5.86	0.96

Key: Coag. = Coagulation; C = Intercept.

Table 4. Coagulation kinetics parameters for *Tectona grandis* and indigo dye effluents

Coagulants	Linearized Lagergren pseudo-first-order						Linearized Lagergren pseudo-second-order				
	$C \times 10^{-3}$ (mg/g)	Slope (mg/gh)	K_1 (h^{-1})	$q_{e\ Cal}$ (mg/g)	R^2	$q_{e\ Exp}$ (mg/g)	$C \times 10^{-3}$ (hg/mg)	Slope $\times 10^{-3}$ (g/mg)	K_2 (g/mgh)	$q_{e\ Cal}$ (mg/g)	R^2
KT	1.73	- 0.91	2.09	54.08	0.92	107.36	0.32	9.24	0.265	108.26	1.00
AT	1.68	- 0.78	1.79	47.75	0.94	106.90	0.37	9.28	0.233	107.79	1.00
KI	1.71	- 0.90	2.07	51.64	0.94	90.25	0.50	10.95	0.242	91.32	1.00
AI	1.74	- 0.90	2.06	54.95	0.94	90.01	0.56	10.96	0.213	91.24	1.00

with the experimental data since the quantity of dye calculated was by far lesser than the quantity of dye coagulated per unit weight of the coagulant obtained in the experiment ($q_{e(cal)} << q_{e(exp)}$) but Largergren pseudo-second-order coagulation kinetic (Fig. 4) did. Equally, pseudo-second-order kinetic fitted well in all the coagulation process since the correlation coefficient R^2 ~ 1 (Table 4), while $R^2 << 1$ in pseudo-first-order kinetic (Table 4). The rate constant K_2 was highest in KT (0.265 g/ mgh), while that of the AI (0.213 g/ mgh) was the lowest, this showed that the coagulation process was fastest in KT and slowest in AI (Minguan, 2009; Hameed *et al.,* 2007; Rakhi and Vankar, 2007).

Coagulation thermodynamics. The plot of log K_o against 1/T gave a straight line graph (Fig. 5) with the intercept and slope used to calculate entropy ΔS and enthalpy ΔH and subsequently the free energy ΔG of the coagulation thermodynamic (Table 3). The value

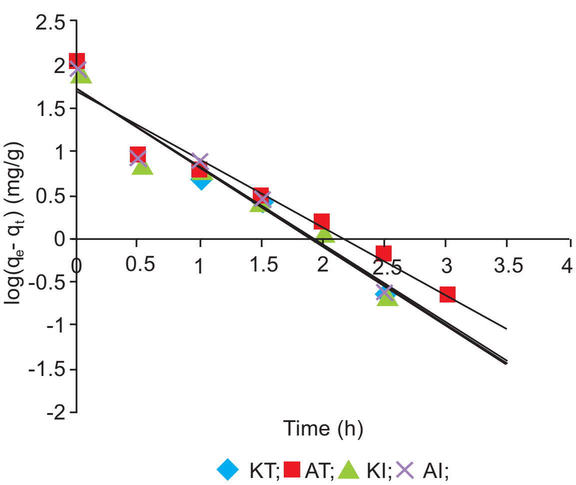

Fig. 3. Linearized Lagergren pseudo-first-order kinetics for the coagulation of *T. grandis* and indigo dye by kaolin and alum.

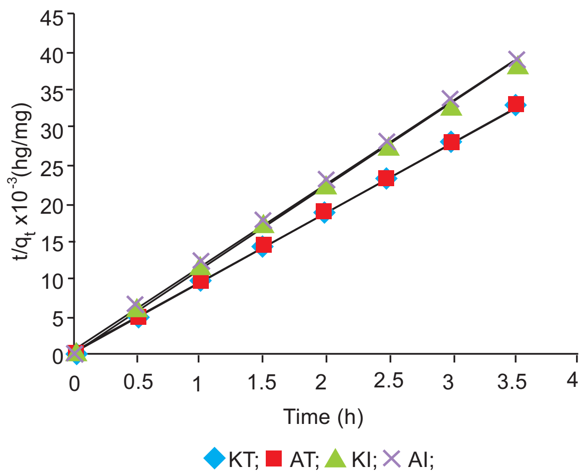

Fig. 4. Linearized Lagergren pseudo-second-order kinetics for the coagulation of *T. grandis* and indigo dye effluents by kaolin and alum.

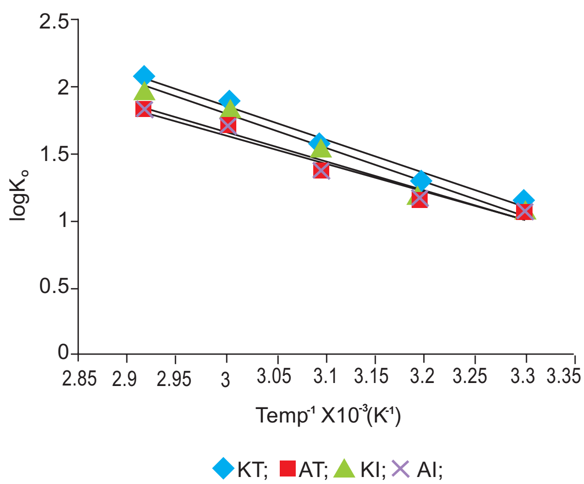

Fig. 5. Van't Hoff plot for the coagulation of *T. grandis* and indigo dye by kaolin and alum.

of ΔH greater than 40 KJ/mol in all the coagulation process indicated that the process is endothermic and chemisorption, while the positive and negative values of ΔS and ΔG are the indication of spontaneity and irreversibility of the process. The correlation coefficients (R^2) were almost equal to unity in all the coagulation processes, evidence that the thermodynamic process fitted quite well with the experimental data.

Conclusion

The study showed that kaolin in place of alum can be used effectively in the removal of both *T. grandis* and indigo dyes from their respective dyeing effluents. The thermo - kinetics parameters for the coagulation process favoured chemisorption and obeyed the Lagergren pseudo-second-order model. Also, the positive values of ΔH and ΔS as well as the negative values of ΔG obtained showed that the interactions of the coagulants with the dye effluents were endothermic, spontaneous and favourable.

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