Kinetic and Thermodynamic Studies of Indigo Adsorption on some Activated Bio-Solids

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Summary: The performances of five activated bio-solids adsorbents on adsorption of Indigo from its dyeing effluent were studied using their thermo-kinetics equilibrium data. The results were compared with the commercial powder carbon as standard. The adsorbents were prepared from cattle bone carbon, algae carbon, water lettuce carbon, elephant grass carbon and crab shell carbon. The activated cattle bone has the highest monolayer adsorption capacity among the bio-solids. The adsorption kinetics of all the adsorbents conformed to the pseudo-second order kinetics, with good correlation. Also, the thermodynamics parameters of the adsorption process fitted very well with the experimental data. The standard Gibb's free energy change (ΔG^o) for all the adsorption reaction was negative, indicating the spontaneity of the process.

Introduction

Wastewaters from dye house usually contain about 10-50 mg/L of dyes in solution with high amounts of surfactants, dissolved solids and possibly heavy metals [1]. The dyes usually changed the colour outlook of the receiving water bodies where they are discharged when not properly adsorbed or treated. It had been reported that activated carbons, either from agro-solid by products or coal are effective pollutants removals from waste waters, because they have excellent adsorption efficiency for organic and mineral pollutants [2-5].

In present study, attention was on the kinetics and thermodynamics parameters of the adsorption of Indigo onto five bio-solid adsorbents [6]. The adsorbents are: cattle bone carbon (ACBC), algae carbon (AAC), water lettuce carbon (AWLC), elephant grass carbon (AEGC) and crab shell carbon (ACS). The highly priced and demanded commercial powdered activated carbon (PAC) was used as standard, in which the performances of the bio-solids were compared. The adsorption process was analysed using equilibrium adsorption isotherms [6-8], Langmuir [9] and Freundlich [10]. The commonly linear regression of least squares method was adopted to estimate the isotherm parameters [1, 11].

Results and Discussion

The calibration curve used for this study is shown in Fig. 1. It was prepared at wavelength of maximum absorption (λ_{max}) 410 nm corresponding to the absorption of leuco-dye (yellow colouration) [12]. It was reproducible and linear over the calibration range and it agrees with the findings of Ncibi *et al.*, [4]. It has been reported that the time-dependent behavior of the indigo dye exhaustion by the cotton fabric showed increasing dye uptake with higher time of dyeing [5, 13].

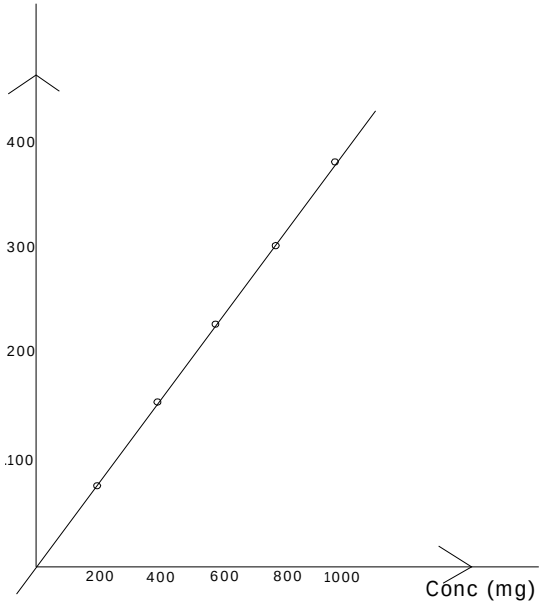

Fig. 1: Caliberation curve.

The non-linear and the linearised expression of the Langmuir, Freundlich isotherms and Lagergren pseudo-first- and second-order kinetics are shown in Table-1. The equations were used to describe the kinetics and the thermodynamic adsorption of the dye on the adsorbents. The reciprocal of dye-uptake, $^1/q_e$, was plotted against the concentration of the residual dye (Indigo) after adsorption with the adsorbent, $^1/C_e$, to obtain the Langmuir isotherm (Fig. 2). The logarithm forms of log q_e versus log C_e were used for Freundlich Isotherms (Fig. 3) [14, 15]. The total number of binding sites, Q_o, available for adsorption and the value of b, energy of adsorption (Table-2), were found to be in the order ACBC>AWLC> AAC>AEGC>ACS for the adsorbents, with ACBC and ACS having the highest and lowest number of

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available sites for adsorption of indigo dye from the dye liquor, respectively. The separation factor, r, was found to be less than unity in all the adsorbents and this indicated favourable adsorption [5]. Its order was a reversal of that of the binding sites above (*i.e.* ACBC<AWLC<AAC<AEGC<ACS). The adsorption isotherms fitted well with experimental data since correlation coefficient, R^2, was almost equal to 1 (Table-2).These also agreed with Manaskorn *et al.*, [14] in removal of reactive dye from aqueous solution. The values of Q_0 and b are higher in ACBC (least separation factor, r) among the bio-solids absorbents, rated next, (57%) to PAC, which was the standard. However, all the activated bio-solids showed high adsorption efficiency [5] and can still be used in place of PAC. Table-3 shows the comparism of the maximum monolayer adsorption capacities of other dyes on various adsorbents with those used in this study. The monolayer adsorption capacity Q was calculated from the inverse of the intercept of Langmuir graphs (Table-4).

Table-1: Absorption isotherms with their linear forms and thermodynamic equation.

Isotherm		Linear form	Plot	Reference
Langmuir	$q_e = Q_o b C_e / (1+ bc_e)$	$1/q_e = 1/Q_o + 1/bQ_oC_e$	$1/q_e$vs $1/C_e$	[7]
Freundlich	$Q = K_fC_e^{(1/n)}$	$\log q_e = \log k_f + {}^1/n \log C_e$	$\log q_e$vs $\log C_e$	[8]
Lagergren Pseudo-first-order	$\frac{dq_t}{dt} = k_1 (q_e - q_t)$	$\log(q_e - q_t) = \log q_e - \frac{Kt}{2.303}$	$\log (q_e - q_t)$ vs t	[6]
Lagergren Pseudo-second-order	$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2$	$\frac{t}{qt} = \frac{1}{k_2q^2_e} + \frac{1}{q_e} t$	t/q_evs t	[6, 11]
Thermodynamic equation (Van't Hoff)	$\text{Log } k_o = \frac{\Delta S^o}{2.303R} - \frac{\Delta H^o}{2.303RT}$		$\log K_o$ vs. ${}^1/_T$	[6, 11]

Key:
C_o = initial concentration of dye. (mg/ L)
q_e = amount of dye adsorbed per unit weight of adsorbents (mg/g)
C_e = equilibrium concentration of the adsorbate (mg/l)
Q_oLangmuir maximum monolayer adsorption capacity(binding sites) (mg/g)
Q_o also the total number of binding sites that are available for sorption.(mg/g)
b Langmuir constant (L /mg)
r = dimensionless separation factor
K_f and n are Freundlich constants, associated with adsorption capacity and adsorption intensity respectively.
K = rate constant
q_e(cal) = calculated dye uptake(.(mg/g)
q_e and q_t = amount of dye adsorbed (mg/g) at equilibrium and at any time, t (hr) respectively
K_1 = equilibrium rate constant of pseudo-first–order adsorption (g/mg hour).
K_2 = equilibrium rate constant of pseudo-second-order adsorption (g/mg hour).
ΔG^o =change in free energy (KJ/mol)
ΔH^o = change in enthalpy (KJ/mol)
ΔS^o = change in entropy (J/molK)

Table-2: Isotherms constants values for the adsorption of Indigo by the activated bio-solid adsorbents.

Adsorbent	Langmuir				Freundlich			Lagergren Pseudo-first-order				Lagergren Pseudo-second-order			
	Q_o(mg/g)	b (l/mg)	r (mg^2/l)	R^2	K_f(mg/g)	n (g^{-1})	R^2	$K_1{}^1/_{(hour)}$	q_e(cal) mg/g	q_e(exp)mg/g	R^2	K_2 (g/mghr)	q_e(cal) (mg/g)	q_e(exp) (mg/g)	R^2
ACBC	571	0.013	0.214	0.997	1.920	1.160	0.998	0.603	5.495	55.87	1.00	0.309	56.88	55.87	1.00
AAC	182	0.011	0.244	0.963	1.520	1.247	0.975	0.921	6.918	53.38	1.00	0.151	55.96	53.38	1.00
AWLC	235	0.012	0.228	0.928	1.820	1.236	0.970	0.778	8.913	54.29	1.00	0.278	55.99	54.29	1.00
AEGC	167	0.010	0.262	0.966	1.470	1.309	0.964	1.071	6.761	51.66	0.79	0.141	54.35	51.66	1.00
ACS	111	0.006	0.371	0.947	-1.280	0.488	0.941	0.935	8.128	44.23	1.00	0.131	47.62	44.23	1.00
PAC	1000	0.014	0.202	0.999	1.940	1.125	0.735	1.227	6.998	55.87	0.76	0.309	59.99	55.87	1.00

Table-3: The comparism of the maximum monolayer adsorption capacities of some dyes on various adsorbents with the agro-solid wastes used in this study.

Dye	Adsorbent	Maximum monolayer adsorption capacities (mg/g)	References
Remazol Red	Activated carbon (300-500 µm)	400.000	[15]
RBBR	Bagasse fly ash	32.468	[11]
Methylene Blue	Rattan saw dust	294.120	[3]
Methylene Blue	Apricot stones-A. Carbon	4.110	[16]
Methylene Blue	Almod shell-Activated Carbon	1.330	[16]
Indigo	Cattle bone – A. Carbon (ACBC)	571.000	
Indigo	Algae – A. Carbon (AAC)	182.000	
Indigo	Water lettuce– A. Carbon (AWLC)	235.000	
Indigo	Elephant grass- A. Carbon (AEGC)	167.000	
Indigo	Crab shell – A.(ACS)	111.000	
Indigo	Commercially Available Powder Activated Carbon(PAC)	1000.000	

Table-4: Adsorption isotherms and thermodynamic's intercepts and slopes of Plotted Graphs.

Adsorbent	Langmuir		Freundlich		Lagergren Pseudo-first-order		Lagergren Pseudo-second-order		Thermodynamics (Van't Hoff)	
	Intercept x10^{-3}	Slope	Intercept (Log)	Slope	Intercept (Log)	Slope	Intercept x10^{-3}	Slope x10^{-2}	Intercept	Slope x10^{3}
ACBC	1.750	0.014	1.920	0.862	0.740	-0.262	1.000	1.758	6.670	-1.588
AAC	5.500	0.048	1.520	0.802	0.840	-0.400	2.100	1.787	3.600	- 0.784
AWLC	4.250	0.035	1.820	0.809	0.950	-0.338	1.400	1.786	5.250	- 1.228
AEGC	6.000	0.058	1.470	0.764	0.830	-0.465	2.400	1.840	3.450	- 0.780
ACS	9.000	0.150	-1.280	2.051	0.910	-0.406	3.900	2.100	1.540	- 0.318
PAC	1.000	0.007	1.940	0.889	0.845	-0.533	0.900	1.667	6.890	- 1.619

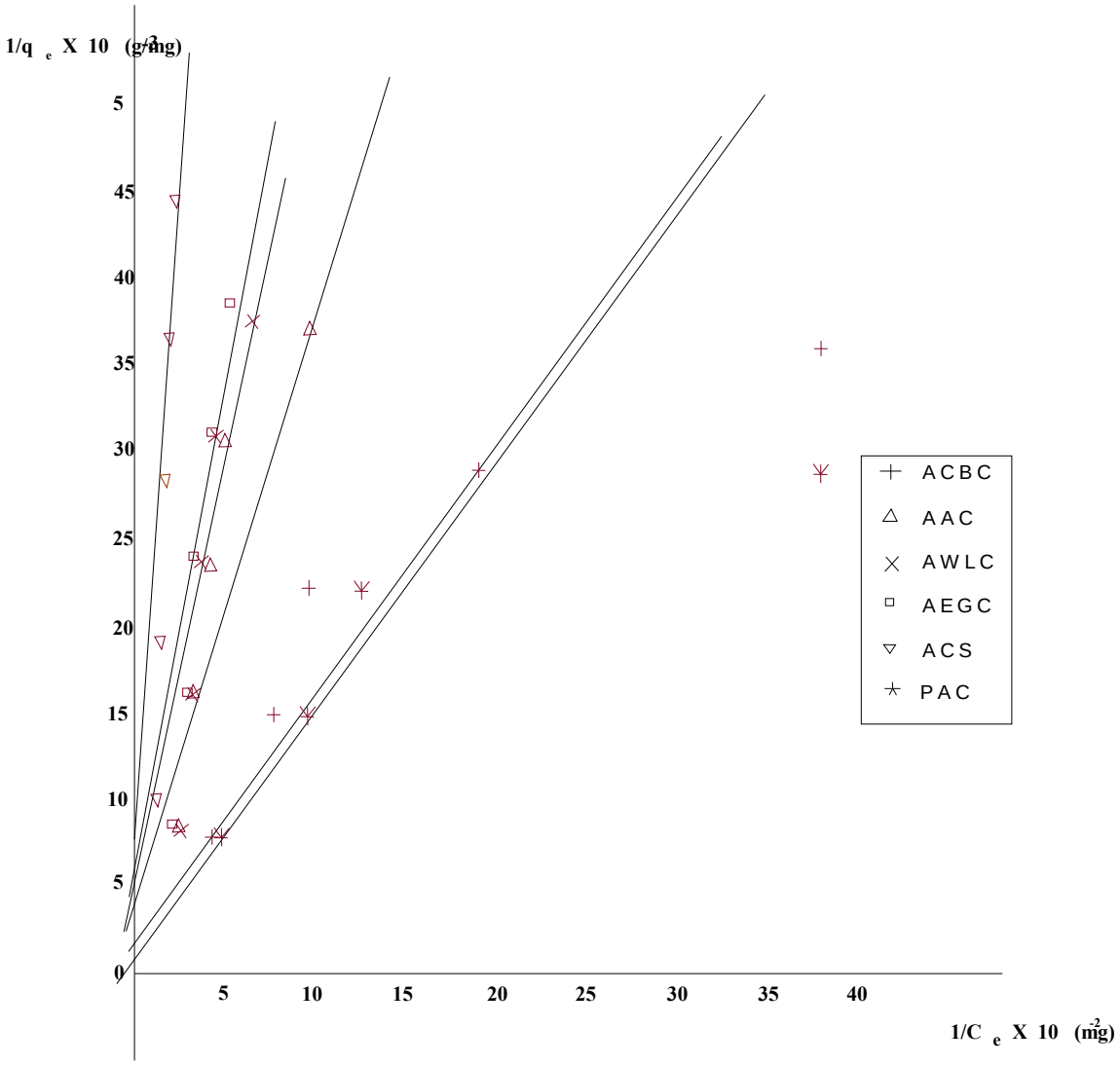

Fig. 2: The linearized Langmuir isotherm for indigo on adsorbents.

The linearized Freundlich isotherm graph (Fig. 3) with the adsorption capacity value, K_f, was found to be in the order ACBC > AWLC > AAC > AEGC > ACS, meaning that ACBC has the highest capacity to remove indigo dye from the dye effluent and with ACS the least. The value of the adsorption intensity, n, was greater than unity (n > 1) in all the adsorbents (except in ACS) and follow the order: ACBC < AWLC < AAC < AEGC < ACS (Table-2). This high value of adsorption intensity also indicated that the adsorbents had good adsorption of the dye from the dyeing effluent. The low value for ACS indicated cooperative adsorption [3].

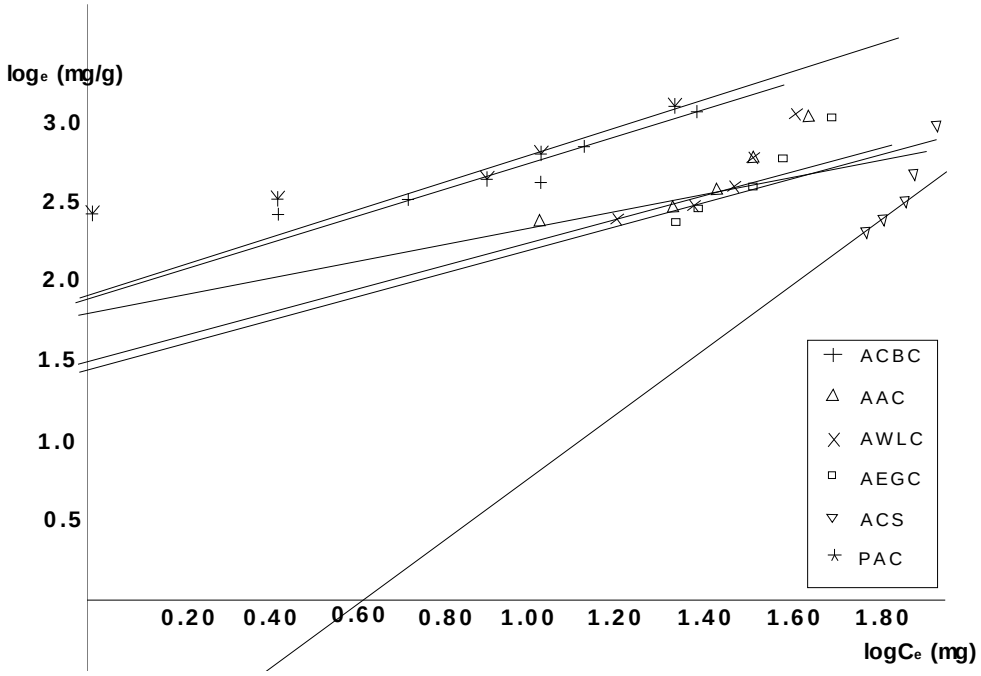

Fig. 3: The linearized Freundlich isotherms for indigo on adsorbents.

The equilibrium dye-uptake, q_e, of the adsorption kinetics was time dependence. They were evaluated and used in plotting the linearized pseudo-first- and second-order kinetics. Straight lines were obtained (Fig. 4 and 5, respectively) and their slopes and intercepts were shown in Table-4. The equilibrium rate constant K is the inverse of time (hr) of Lagergren pseudo-order adsorption kinetic and it was calculated from the slope of the graph [7]. Data obtained from Lagergren pseudo-first-order adsorption kinetic (Fig. 4) does not fit well with the calculated one but Lagergren pseudo-second-order adsorption kinetic does (Fig. 5) [4]. The rate constant K_2, as well as the calculated dye-uptake (q_e (cal) for ACBC in pseudo-second-order kinetics were found to be the highest in ACBC (Table-2) among the bio-solid adsorbents while that of ACS was the least. This shows that the rate of the reaction was fastest with ACBC and slowest with ACS. Hence, the quantity of dye adsorbed (q_e) from the effluent with ACBC adsorbent was the highest and lowest in ACS. However, the correlation coefficient, R^2, of the pseudo-order reactions of the adsorbents varied. It fitted well with the experimental data of the second-order kinetic ($R^2 = 1$) while in first-order, it was less than unity ($R^2 < 1$) for powder activated carbon (PAC).

The Van't Hoff's plot for the adsorption thermodynamic (Fig. 6) was obtained when the values of the thermodynamic equilibrium constant, Log $K_{o,}$ was plotted against 1/T (K^{-1}) [14]. Table-5 shows the thermodynamic parameters of the plot. The values were expressed in Joule per moles as this is the unit of enthalpy. It was calculated from the slopes and intercepts of the graphs using the Vant't Hoff's expression in Table-1. It fitted quite well with the experimental data since its correlation coefficient R^2 is equal to unity ($R^2 = 1$) in all the adsorbents. The positive values of ΔH^o show the endothermic nature of the adsorption and that the nature of the adsorption was possibly that of physical adsorption (Physisorption).

Table-5: The Values of Van't Hoff enthalpy ΔH^o, entropy ΔS^o and Gibb's free energy ΔG^o for the adsorption process.

Van't Hoff thermodynamic parameters.

Adsorbent	ΔH^o ($KJMol^1$)	ΔS^o ($JMol^{-1}K^1$)	ΔG^o ($KJMol^1$)	Temp (K)	R^2
ACBC	30.354	127.496	-8.277	303	1.000
AAC	14.986	68.814	-5.865	303	1.000
AWLC	24.429	100.353	-5.978	303	1.000
AEGC	14.910	65.964	-5.072	303	1.000
ACS	6.079	29.437	-2.840	303	1.000
PAC	30.947	131.702	-8.959	303	1.000

The negative and positive values of ΔG^o and ΔS^o shows the spontaneity of the dye adsorption and the randomness at the adsorbent-dye effluent interphase respectively [16-21]. The negative value of ΔG^o also indicated that the adsorption process was highly favourable for the dye.

Experimental

Materials

The bio-solids mentioned above were used and they were all obtained from Nigeria except Alga, which was obtained from Fluvani Distrite, Orisa State, India. The materials were processed into activated carbons and made to adsorb indigo from a dyeing effluent [5]. The indigo dye (BASF product) was purchased from a dyestuff marketer in Lagos, Nigeria. It was in a solid form and its purity was checked using standard methods. Chemicals and equipment used were of analytical grade and obtained from Chemistry Department, The Federal University of Technology, Akure, Nigeria.

Preparation of Activated Carbons from Bio-Solids

Activated carbon adsorbents were prepared from the following materials: cattle bone (ACBC), algae (AAC), water lettuce (AWLC), elephant grass (AEGC) and crab shell (ACS). The materials were washed with hot distilled water to remove dust and other impurities and sun dried. The cattle bone and crab shell were carbonized in an oven at 250 °C for 3 hrs while algae, water lettuce and elephant grass were carbonized at 150 °C for 3 h. After cooling at room temperature, the absorbents were ground to 500-700 μm. Each of the adsorbents was impregnated with 0.1M tetraoxosulphate (VI) acid in ratio 1:1 and dried at 150 °C for 24 h [3, 4]. The carbonized adsorbents were cooled to room temperature, washed with distilled water and dried at 105 °C for 2 hrs. Thereafter, they were soaked in 0.01M sodium bicarbonate (0.01 M $NaHCO_3$) solution for 8 h, followed by washing and drying as done previously. All the adsorbents were then ground and sieved to 400 μm mesh size.

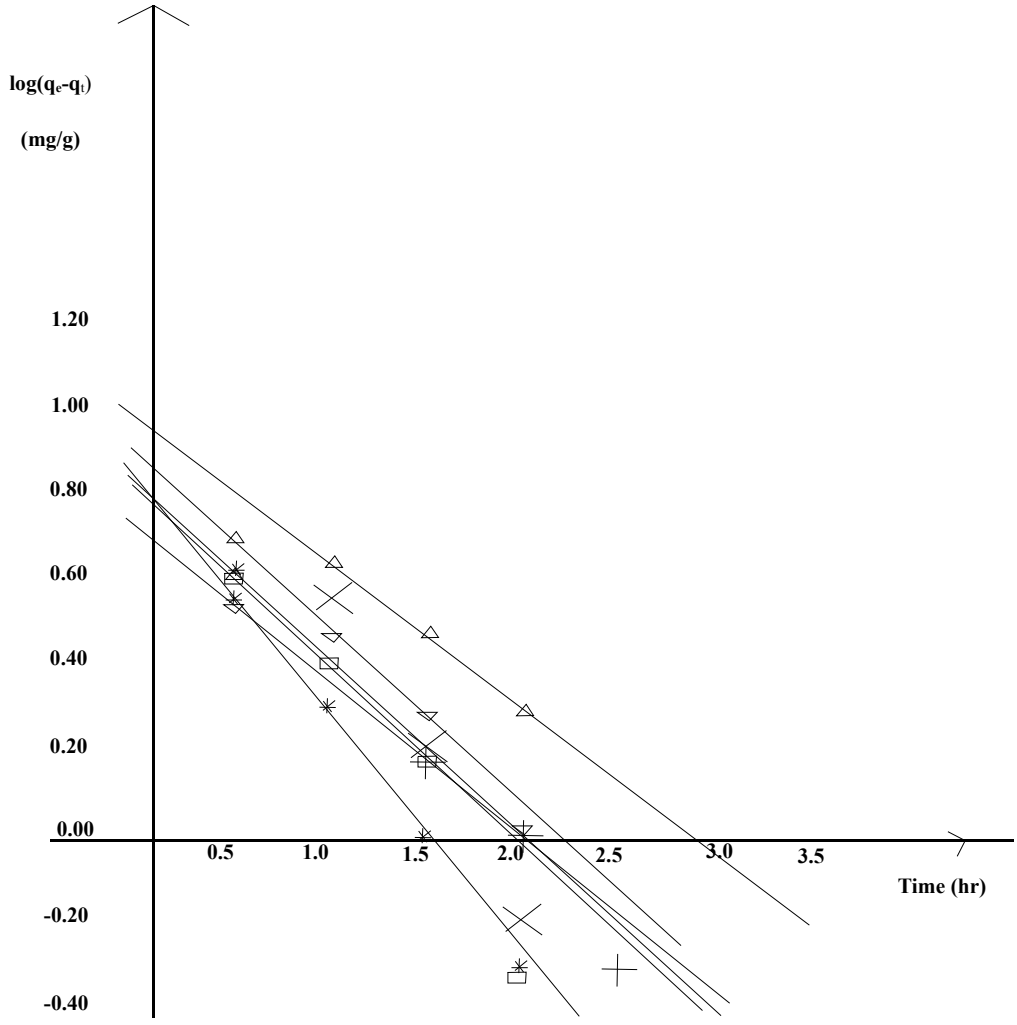

Fig. 4: The linearized Lagergren Pseudo-first –order kinetics for the adsorption of indigo on adsorbents.

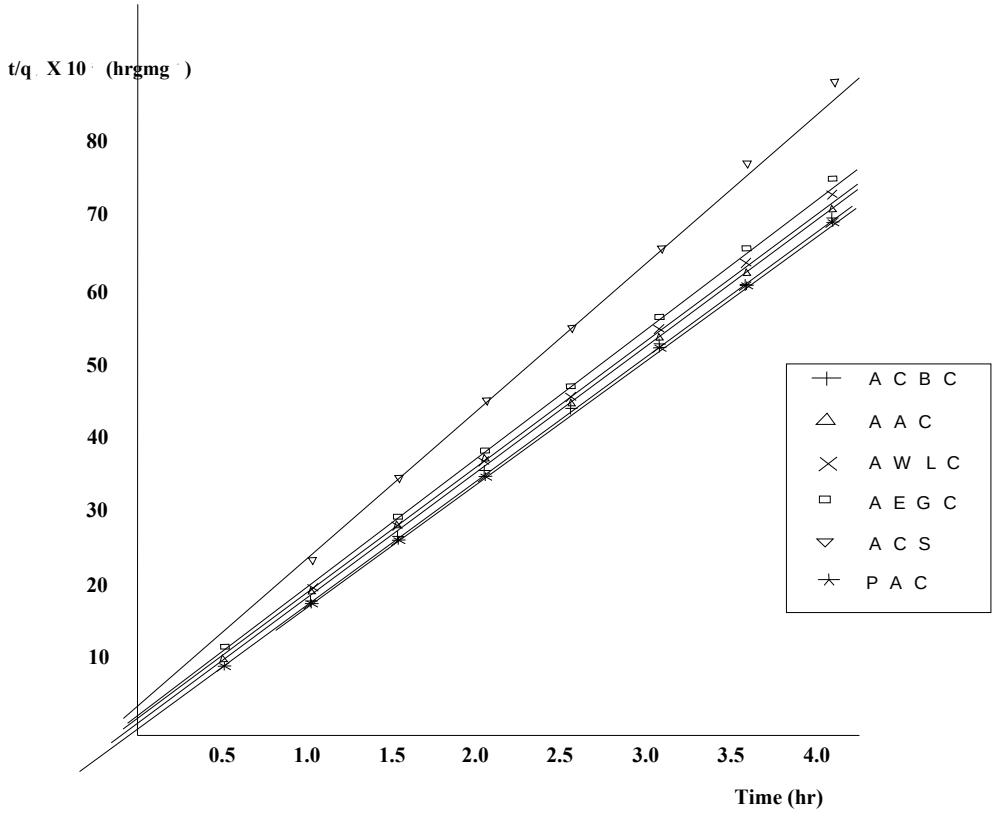

Fig. 5: The Pseudo- second-order kinetics for the adsorptions of indigo on adsorbents.

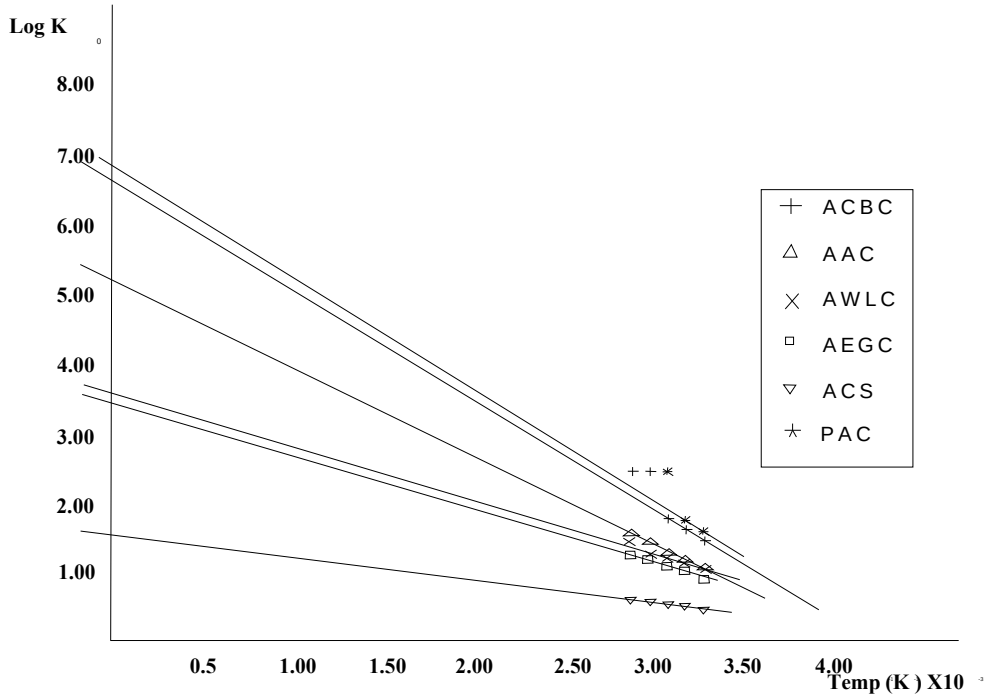

Fig. 6: The Van't Hoff plot for the adsorption of indigo on adsorbents.

Preparation of Indigo Dye-Liquor and Dyeing

1 g Indigo was accurately weighed into 250 mL conical flask and 20 mL of 96% ethanol was added to make a paste. A solution containing 500 mg of $Na_2S_2O_4$, 100 mg of NaCl and NaOH were added to the paste, stirred and heated to 60 °C for total dissolution and reduction of the dye to its leuco-form (clear yellow colouration shown) [12]. The dissolved dye solution was transferred to standard flask and made up to a litre mark with distilled water. The dye was standardized on Uv-Visible Spectrophotometer (Pharmacia LKB Biochrome 4060). Its wavelength at maximum absorption (λ_{max}) was found to be 410 nm and this was used to measure the absorbance of various concentrations (0, 0.2, 0.4, 0.6, 0.8, 1.0 g) of the dye to ascertain compliance with Beer-Lambert's law. Subsequently, absorbance of the dye solutions used for dyeing the fabrics and the residual dye baths (effluent) were measured to provide means of evaluating the amount of dye adsorbed by the fabrics [22].

2% dyeing depth of the fabric was carried out. The dyeing was done in a dyeing machine IIBM. 100 mL of prepared dye solution of liquor ratio 20:1 was measured accurately into each of the 6 cups of the dyeing machine and 5 g each of the pretreated fabric introduced [22]. The dyeing was done at 60 °C and 100 rpm. Analysis of the residual dyeing liquor, after cooling, was carried out at 15 mins dyeing intervals. The dyeings (dyed cotton fabrics) were washed with cold water and air dried for oxidation of the dye. The residual dye baths (effluent) were used for the absorption study.

Adsorption Study

Batch technique was used for the adsorption studies using the dyeing machine with its 6 dyeing cups of 250 mL capacity each. The dyeing effluents were shaken with the above prepared adsorbents one after the other at 100 rpm. The performances of these adsorbents were compared with the commercially available powdered activated carbon (PAC), which was also subjected to the same treatment as other adsorbents. The contact time of adsorbents with effluent, temperature and adsorbent dosage were varied in the study.

Effect of Adsorbent Dosage/ Contact Time and Temperature

The percentage of the dye adsorbed by the adsorbents was determined by weighing various amount of each adsorbent ranging from 0.0-1.0 g into the dyeing cups labeled 1-6, respectively of the dyeing machine. In each of the dyeing cup was previously contained 100 mL of the residual dye **(**282 mg/l). The dyeing machine was allowed to run at 303 K, for 100 mins and at 100 rmp [14]. In case of contact time and temperature variations, 0.5 g of each adsorbent was added to the same quantity of dye solution as for adsorbent dosage. The contact time of adsorbent and effluent was varied from 0.0 h to 4.0 hrs at a constant temperature of 303 K. Assessment of the dye adsorbed under this study was made at every 30 mins. For temperature variation study (from 303-343 K.), a fixed contact time of 1^2/3hrs per cycle was adopted and assessment of the dye adsorbed was done at every 10 K intervals. At the end of each cycle in each of the above test, the cups had their contents filtered for two consecutive times using whatman filter paper and the absorbance of the filtrates were read at 410 nm against reagent blank in Uv-Visible spectrophotometer to determine the quantity of the dye left in the wastewater [14, 17]. The kinetics and the thermodynamic parameters of the study were evaluated from the results obtained using the relevant equations showed on Table-1.

Conclusion

The activated bio-solids adsorbents in this study adsorbed Indigo from its dyeing effluent very well. The kinetics and the thermodynamics parameters of the adsorption process fitted very well with the experimental data, particularly that of the Pseudo-second-order kinetics.

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