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Equilibrium, Kinetic and Optimization Studies for the Adsorption of Tartrazine in Water onto Activated Carbon from Pecan Nut Shells

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Abstract A series of experimental studies has been carried out using a novel, sustainable adsorbent to remove Tartrazine dye, namely, a steam activated carbon obtained from pecan nut shells. The dye also known as acid yellow 23 has been used in the food industry but is now classified as a carcinogen. The experimental equilibrium data has been used to test four equilibrium isotherm models and then the best fitting model was optimised to minimise the mass of adsorbent used to save costs in industrial applications using a two-stage batch adsorption system. The experimental contact time data has also been modelled and the best fit model has been used to optimise/minimise the contact time for a range of process conditions.

Keywords Pecan nut shell biomass · Active carbon · Tartrazine dye adsorption · Dye wastewater treatment

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1 Introduction

There are thousands of various chemicals and other toxic substances in effluents discharged by industry. These contain organic and inorganic pollutants, which cause deoxygenation by promoting microbial activity, or material that is directly toxic to the lives in aquatic and human ecosystems. Therefore, it is of significant importance to treat these wastewaters (McKay 1995).

Coloured dyes are important pollutants that make up the wastewater body. The textile industry discharges a large number of coloured effluents annually. Approximately 2% of produced dyes and colourants are discharged in effluents of the total annual world dye production of over 700,000 t. The dyes in wastewaters bring both detrimental aesthetic effects and some are toxic or even carcinogenic. Reactive acidic dyes are widely used in the textile and other industries due to the increasing use of cellulosic fibres. Common methods for the treatment of textile effluents include adsorption, coagulation, advanced oxidation, flocculation and biological treatment. Adsorption is widely recognised as an effective method for the wastewater treatment (Pereira et al. 2003).

Adsorption is growing in popularity due to its potential for rapid treatment and the fact that it can produce a very high quality treated water. It is a method to treat wastewater in a sufficient and reasonably low cost. The selection of the adsorbent is the key factor to control the efficiency and operational cost of the treatment plant. An ideal adsorbent should have a large adsorption capacity, a fast adsorption rate, low raw material and production cost, and can be regenerated and reused easily (McKay 1995).

Adsorption processes are characterised by the adsorption kinetics and an adsorption equilibrium isotherm. Both isotherm and kinetic data are important tools to understand the mechanisms of adsorption and are necessary for the design of adsorption treatment plant (Ip et al. 2010).

Tartrazine adsorption has been carried using hen feather, chitosan (Saime et al. 2010) melamine formaldehyde-tartaric acid adsorbent, coconut husks, fly ash, saw dust, bagasse, and biomass such as fungus and algae (Fauzia et al. 2015).

Commercially available activated carbon (AC) adsorbents (Robinson et al. 2001) are usually derived from natural materials such as wood, coconut shell, lignite or coal, but almost any carbonaceous material may be used as precursor for the preparation of carbon adsorbents. Because of its availability and cheapness, coal is the most commonly used precursor for AC production (Rozada et al. 2003). Coal is a mixture of carbonaceous materials and mineral matter, resulting from the degradation of plants. The sorption properties of each individual coal are determined by the nature of the original vegetation and the extent of the physical–chemical changes occurring after deposition. Coal-based sorbents have been used (Karaca et al. 2004; Venkata et al. 2002; McKay et al. 1999) with success for dye removal. However, since coal is not a pure or sustainable material, it has a variety of surface properties and thus different sorption properties.

Plentiful renewable agricultural biomass raw materials are available for adsorption and active carbon production; these include wood (Poots et al. 1976), bagasse pith (McKay 1998; McKay et al. 1997; Chen et al. 2001; Valix et al. 2004; Chan et al. 2009). Bamboo Mui et al. 2010a, b), biomass and agrowaste (Cha et al. 2016), chickpeas (Habila et al. 2015), hickory biochars (Pezoti et al. 2014), kudzu (Nadeem et al. 2006), pine cones (Ding et al. 2016, Allen et al. 2004; Hadi et al. 2011) and rice husk (Wang et al. 2015). Other forms of natural wastes which have been used for textile dye removal include chitosan from seafood shell waste (Abbasi and Habibi 2016; Cho et al. 2015) and hydroxyapatite (Lemlikchi et al. 2015) from bone char. These waste materials have little or no economic value and often present a disposal problem. Therefore, there is a need to valorise these low-cost by-products. Consequently, their conversion into activated carbons or alternative adsorbents would add economic value, help reduce the cost of waste disposal and most importantly provide a potentially inexpensive alternative to the existing commercial activated carbons.

Table 1 Adsorption isotherm models and the corresponding equations

Model	Equation	Reference
Langmuir isotherm	$q_\mathrm{e} = \frac{q_\mathrm{m} K_\mathrm{L} C_\mathrm{e}}{1+K_\mathrm{L} C_\mathrm{e}}$ (1)	Langmuir 1908
Freundlich isotherm	$q_\mathrm{e} = K_\mathrm{F} C_\mathrm{e}^{\frac{1}{n}}$ (2)	Freundlich 1906
Langmuir-Freundlich isotherm	$q_\mathrm{e} = \frac{q_\mathrm{m} K_\mathrm{LF} C_\mathrm{e}^{\frac{1}{n_\mathrm{lf}}}}{1+K_\mathrm{LF} C_\mathrm{e}^{\frac{1}{n_\mathrm{lf}}}}$ (3)	Sips 1948
Redlich-Peterson isotherm	$q_\mathrm{e} = \frac{q_\mathrm{m} K_\mathrm{R} C_\mathrm{e}}{1+K_\mathrm{R} C_\mathrm{e}^{\beta}}$ (4)	Redlich and Peterson 1959

Other agricultural solid wastes from cheap and readily available resources such as date pits (Banat et al. 2003), durian seed (Ahmad and Ahmad 2014) pith (Ho and McKay 1999a, b; McKay et al. 1987), waste biomass (Dawood et al. 2013), corn-cob (Robinson et al. 2002), barley husk (Robinson et al. 2002), walnut shell (Heibati et al. 2014), pine cone (Sen et al. 2011), wheat straw and wood chips have also been successfully employed for the removal of dyes from aqueous solution. In the present study, we have produced novel activated carbons from pecan nut shells using steam activation and applied this carbon to remove tartrazine from wastewater. In this work, a series of experimental studies has been carried out using an alternative activated carbon adsorbent for the removal of tartrazine dye. The activated carbon was obtained from an agricultural precursor (pecan nut shells) (NAC-857-H2O). The equilibrium modelling is very important to explore the capacity of the adsorbents. The experimental equilibrium data was used to test four equilibrium isotherm models

Table 2 Values of k_2, q_e, and n in pseudo-second kinetic model equation

C_0	k_2	R^2	q_e
10	0.00928	0.956	4.70
20	0.00981	0.975	7.33
30	0.00557	0.967	10.9
40	0.00510	0.984	13.2
50	0.00262	0.982	17.5
60	0.00207	0.992	21.1

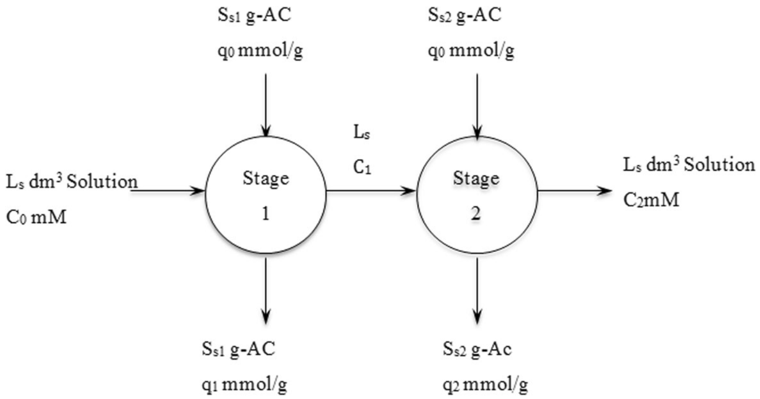


Fig. 1 Schematic flowchart of two-equilibrium-stage operation

to find out which model fits the best and then the best fitting model is used to minimise the mass of adsorbent used so as to save money in industry application. Besides, the kinetic modelling of the batch contact time data is extremely important to predict the optimum design of batch adsorbents to remove pollutants from effluents. The experimental contact time data was used to test a set of kinetic models to establish which model fits the data best and fits the mechanistic system the best. The contact time was optimised as well.

2 Experimental Section

2.1 Raw Materials

The pecan nuts shells from *Carya illinoinensis* were obtained from local producers in Chihuahua, Mexico. The shells presented a light brown coloration; they were dried in an oven at 105 ± 5 °C and then they were cracked into fragments between 0.5 and 1 cm of diameter and they were used in those conditions for carbonisation or activation process. A simple characterisation of the raw materials prior carbonisation and activation process was performed and the thermal characteristics were measured by TGA analysis (SDT Q600). About 2 mg of sample material was heated from 25 to 700 °C until no further weight loss was detected. Also moisture and total ash contents were determined.

Table 3 Summary of equilibrium isotherm constants of tartrazine acid yellow 23 dye for different isotherms

Langmuir isotherm			
K_L	q_m	–	SSE
0.01406	46.37	–	1.125
Freundlich isotherm			
K_F	$1/n$	–	SSE
1.059	0.7493	–	0.2087
Langmuir-Freundlich isotherm			
q_m	K_{LF}	$1/n_{lf}$	SSE
64.2	0.013	0.892	0.6076
Redlich-Peterson isotherm			
q_m	K_R	β	SSE
26.5	0.02589	0.871	0.9353

2.2 Characteristics of the Adsorbate

Tartrazine, also named acid yellow 23, is widely used as colourant in food, drugs and cosmetics. It is now designated as carcinogenic and causing allergic reactions (National Centre for Biotechnology Information 2015).

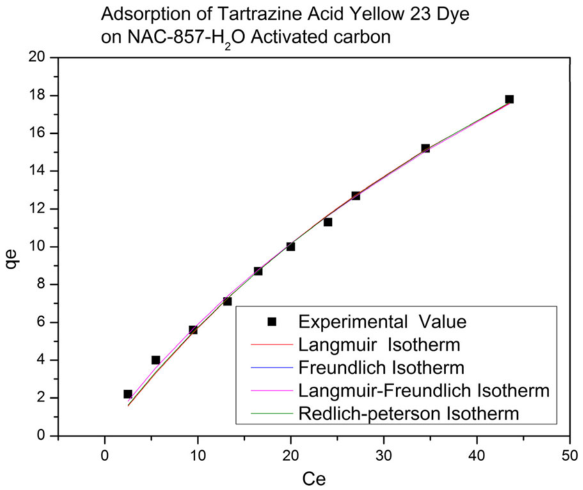


Fig. 2 Equilibrium isotherms for tartrazine acid yellow 23 dye system

Table 4 Minimum total adsorbent mass $S_{s1} + S_{s2}$ for removal of tartrazine acid yellow 23 dye using Langmuir-Freundlich isotherm ($C_2 = 1\%\ C_0$)

C_0 (mg/L)	C_1 (mg/L)	C_2 (mg/L)	S_{s1} (g-AC)	S_{s2} (g-AC)	$S_{s1} + S_{s2}$
4.7	0.51	0.047	1.16	1.06	2.21
9.5	6.91	0.095	0.074	8.34	8.42
15.1	8.75	0.151	0.15	6.97	7.12
20.3	2.19	0.203	1.38	1.24	2.62
25.2	2.72	0.252	1.42	1.27	2.69
30	3.24	0.300	1.45	1.29	2.75
35.3	3.82	0.353	1.49	1.32	2.81
39.7	4.29	0.397	1.51	1.34	2.85
49.7	5.37	0.497	1.57	1.37	2.94
61.3	6.63	0.613	1.62	1.40	3.03

It has a molecular formula as $C_{16}H_9N_4Na_3O_9S_2$, it is water soluble and it has a mass of 534.4 g/mol. It is found in certain brands of fruit squash, fruit cordial, coloured fizzy drinks, instant puddings, cake mixes, custard powder, soups, sauces, ice cream, ice lollies, sweets, chewing gum, marzipan, jam, jelly, marmalade, mustard, yoghurt and many convenience foods together with glycerine, lemon and honey products. It is cheaper than beta carotene and therefore used as an alternative to beta carotene to achieve a similar colour. Tartrazine is also reputed to catalyse hyperactivity and other behavioural problems, asthma, migraines, thyroid cancer, etc. Because of its recently attributed hazardous health effects, foods and drinks containing Tartrazine are now avoided. It is a bright orange-yellow powder. In water, the solubility is 20.0 g/100 mL at 25 °C (2.0×10^5 mg/L). The spectral property is 425 nm in water for the maximum absorption waveband.

2.3 Activated Carbon Production

The pecan nut shells and peanut hulls were dried for 24 h and then were heated at 10 °C $\min^{-1}$ up to 857 °C under a nitrogen flow rate (0.5 L $\min^{-1}$); the maximum temperature was selected because that temperature value was very closer to that one reported for activated carbons prepared from another agricultural by-product. After the desired temperature was reached, steam was introduced into the furnace equipped with a quartz reactor, the steam activation was performed by injection of water with a peristaltic pump at the entrance of the quartz vessel (0.7mL $\min^{-1}$) for 80 min; the water drops were carried into the reactor by the gas used to maintain the inert atmosphere (N_2). Then, heating was stopped and the samples were left to cool under the nitrogen atmosphere in the reactor. These conditions were optimised from a previous study (Torres-Pérez et al.

Table 5 Minimum total adsorbent mass $S_{s1} + S_{s2}$ for removal of tartrazine acid yellow 23 dye using Langmuir-Freundlich isotherm ($C_2 = 5\%\ C_0$)

C_0 (mg/L)	C_1 (mg/L)	C_2 (mg/L)	S_{s1} (g-AC)	S_{s2} (g-AC)	$S_{s1} + S_{s2}$
4.7	6.89	0.235	0.0628	3.638	3.57
9.5	2.21	0.475	0.552	0.508	1.06
15.1	3.51	0.755	0.588	0.536	1.12
20.3	4.72	1.01	0.614	0.555	1.17
25.2	5.86	1.26	0.635	0.570	1.21
30	6.98	1.50	0.654	0.582	1.24
35.3	8.21	1.76	0.673	0.594	1.27
39.7	9.24	1.98	0.687	0.603	1.29
49.7	11.56	2.485	0.718	0.621	1.34
61.3	14.26	3.065	0.749	0.639	1.39

Table 6 Minimum total adsorbent mass $S_{s1} + S_{s2}$ for removal of tartrazine acid yellow 23 dye using Langmuir-Freundlich isotherm ($C_2 = 10\%\ C_0$)

C_0 (mg/L)	C_1 (mg/L)	C_2 (mg/L)	S_{s1} (g-AC)	S_{s2} (g-AC)	$S_{s1} + S_{s2}$
4.7	1.52	0.47	0.332	0.312	0.644
9.5	3.08	0.95	0.365	0.338	0.703
15.1	4.89	1.51	0.390	0.358	0.748
20.3	6.58	2.03	0.409	0.372	0.781
25.2	8.18	2.52	0.424	0.382	0.807
30	9.73	3.00	0.438	0.392	0.829
35.3	11.4	3.53	0.452	0.401	0.853
39.7	12.9	3.97	0.463	0.407	0.871
49.7	16.1	4.97	0.486	0.421	0.908
61.3	19.9	6.13	0.511	0.436	0.947

2015) and designed to follow a sustainable production process with the utilisation of local and abundant resources, a direct activation process was used and the activating agent was totally innocuous (water).

The steam activated material was called NAC-857-H_2O for the one prepared at 857 °C with steam activation. After the carbonisation process was finished, the materials were crushed in a hammer mill and the particles were sieved, the particle sizes used for tartrazine removal experiments were between 0.50–1.00 mm; this step was done in order to obtain similar particle sizes to those of granular commercial activated carbons. This fraction was washed with distilled water (10 g L^{-1}) until the pH remained constant, finally they were filtered and dried at 105 ± 5 °C with mass yields around 33.6%.

2.4 Adsorption Isotherms

Batch adsorption isotherms were conducted with 125 mL of synthetic solutions from 10 to 50 mg L^{-1} of tartrazine dye and 0.125 g of carbonaceous materials. The bottles were sealed and placed on an orbital shaker for 5 days at 20 °C. After shaking, the equilibrium pH was measured and recorded, the samples were decanted and the concentration of tartrazine in the aqueous media was determined by UV/Vis with a spectrophotometer (7315, Jenway®). Analytical measurements were obtained with a quantification limit of 0.2 mg L^{-1} and a detection limit of 0.1 mg L^{-1}. It has been verified, that no dye adsorption occurs on the wall of the plastic bottles.

2.5 Equilibrium Isotherm Models

When the amount of solute, being adsorbed, onto the adsorbent is equal to the amount being desorbed, equilibrium is established and the equilibrium solution concentration remains unchanged. Plotting solid phase concentration against liquid phase concentration graphically generates the equilibrium isotherm. The equilibrium

Table 7 Minimum total adsorbent mass $S_{s1} + S_{s2}$ for removal of tartrazine acid yellow 23 dye using Langmuir-Freundlich isotherm ($C_2 = 0.5$ ppm)

C_0 (mg/L)	C_1 (mg/L)	C_2 (mg/L)	S_{s1} (g-AC)	S_{s2} (g-AC)	$S_{s1} + S_{s2}$
4.7	1.57	0.5	0.319	0.299	0.619
9.5	2.26	0.5	0.537	0.494	1.03
15.1	2.89	0.5	0.735	0.668	1.40
20.3	3.37	0.5	0.891	0.803	1.69
25.2	3.77	0.5	1.02	0.916	1.94
30	4.13	0.5	1.14	1.02	2.16
35.3	4.50	0.5	1.26	1.12	2.38
39.7	4.79	0.5	1.36	1.20	2.56
49.7	5.39	0.5	1.56	1.36	2.93
61.3	6.016	0.5	1.78	1.54	3.32

Table 8 Minimum total adsorbent mass $S_{s1} + S_{s2}$ for removal of tartrazine acid yellow 23 dye using Langmuir-Freundlich isotherm ($C_2 = 1$ ppm)

C_0 (mg/L)	C_1 (mg/L)	C_2 (mg/L)	S_{s1} (g-AC)	S_{s2} (g-AC)	$S_{s1} + S_{s2}$
4.7	2.19	1	0.191	0.181	0.372
9.	3.16	1	0.353	0.327	0.680
15.1	4.02	1	0.501	0.458	0.959
20.3	4.69	1	0.619	0.559	1.18
25.2	5.25	1	0.719	0.645	1.36
30	5.75	1	0.810	0.721	1.53
35.3	6.26	1	0.903	0.798	1.70
39.7	6.66	1	0.976	0.859	1.83
49.7	7.49	1	1.13	0.985	2.12
61.3	8.36	1	1.29	1.11	2.41

isotherm equations in Table 1 show the relationship between the concentration of a solute in the fluid (wastewater) phase and the concentration on the solid phase (adsorbent). It is the most convenient and direct way to investigate the adsorption capacity for an adsorbent to an adsorbate (Ip et al. 2010).

The isotherm Eqs. (1) to (4) are presented in Table 1 and the assumptions underlying the four models and the method of analysis have been presented previously (Ho et al. 2002).

2.6 Sorption Kinetics

Batch contact time experiments were conducted at room temperature (20 °C) by stirring 0.5 g of the pecan nut derived carbonaceous materials with 500 mL of tartrazine solutions (50 mg L^{-1}) for NAC-857-H_2O at 150 rpm; the initial concentration was established in order to have a representative and similar dye presence in water than those found in food and cosmetic industry wastewaters. Initial pH values were close to 7.0 in both cases and were recorded at the end of the experiment. The equilibrium time was considered accomplished when no more changes occurred at the X-axis by plotting C_t versus time (t). The tartrazine azo dye concentrations in the solutions were determined using a Jenway® UV/Visible spectrophotometer Model 7315 at 425 nm, the maximum adsorption wavelength of the dye.

2.7 Batch Adsorption Kinetics Models

In order to investigate the mechanism of adsorption and potential rate controlling steps such as chemical reaction, diffusion control and mass transport processes, kinetic models have been used to test experimental data. The kinetic models for batch adsorption can be divided into two categories: (i) pseudo-kinetic chemical reaction controlled models and (ii) mass transfer controlled models. In the present study two kinetic models have

Table 9 Minimum total adsorbent mass $S_{s1} + S_{s2}$ for removal of tartrazine acid yellow 23 dye using Langmuir-Freundlich isotherm ($C_2 = 2$ ppm)

C_0 (mg/L)	C_1 (mg/L)	C_2 (mg/L)	S_{s1} (g-AC)	S_{s2} (g-AC)	$S_{s1} + S_{s2}$
4.7	3.08	2	0.092	0.089	0.181
9.5	4.42	2	0.212	0.199	0.412
15.1	5.61	2	0.324	0.298	0.622
20.3	6.54	2	0.413	0.375	0.788
25.2	7.32	2	0.489	0.439	0.928
30	8.01	2	0.557	0.497	1.05
35.3	8.72	2	0.629	0.555	1.18
39.7	9.27	2	0.684	0.601	1.28
49.7	10.4	2	0.803	0.696	1.50
61.3	11.6	2	0.930	0.796	1.72

Table 10 Minimum total adsorbent mass $S_{s1}+S_{s2}$ for removal of tartrazine acid yellow 23 dye using Langmuir-Freundlich isotherm ($C_2 = 5$ ppm)

C_0 (mg/L)	C_1 (mg/L)	C_2 (mg/L)	S_{s1} (g-AC)	S_{s2} (g-AC)	$S_{s1}+S_{s2}$
4.7	4.85	5	0.0057	0.0057	0.0114
9.5	6.91	5	0.0742	0.0717	0.146
15.1	8.75	5	0.149	0.141	0.291
20.3	10.2	5	0.211	0.195	0.406
25.2	11.4	5	0.263	0.240	0.503
30	12.4	5	0.311	0.280	0.591
35.3	13.5	5	0.361	0.321	0.682
39.7	14.4	5	0.400	0.353	0.754
49.7	16.2	5	0.485	0.419	0.905
61.3	18.0	5	0.575	0.489	1.06

been selected to describe the adsorption kinetics and are represented by Eqs. (5) and (6).

2.8 Pseudo-First-Order Kinetic Model (Lagergren 1898)

$$\frac{dq_t}{dt_t} = k_1(q_e - q_t) \tag{5}$$

Pseudo-second order kinetic model (Ho and McKay 1999a, b)

$$\frac{dq_t}{dt_t} = k_2(q_e - q_t)^2 \tag{6}$$

Integrating and rearranging (6) provides Eq. (7):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{7}$$

If the pseudo-second-order equation is applicable, the plot of t/q_t against t in Eq. (7) should give a linear relationship. This equation provides an advantage that the adsorption capacity of q_e can be obtained from the slope of the linear plot. The applications of this model are widely used in fitting the kinetic data for various systems (McKay and Ho 1999; Ho et al. 2000); the values are shown in Table 2.

2.9 Batch Optimization Model-Activated Carbon Mass

A single-stage adsorption operation, can seldom achieve the desired level of adsorbate removal although single-stage operation has high operating flexibility. A multistage process, i.e. smaller separate batches of adsorbent with filtration between each stage, is more desirable in order to enhance the carbonaceous material efficiency, minimise the total amount of AC used and make the process more economic. The more the batches, the greater the savings are. However, the filtration expense and handling cost are also higher. It is therefore seldom economical to use more than two stages. It is necessary to determine the minimum amount of

Table 11 Minimum total adsorbent mass $S_{s1}+S_{s2}$ for removal of tartrazine acid yellow 23 dye using Langmuir-Freundlich isotherm ($C_2 = 10$ ppm)

C_0 (mg/L)	C_1 (mg/L)	C_2 (mg/L)	S_{s1} (g-AC)	S_{s2} (g-AC)	$S_{s1}+S_{s2}$
4.7	6.88	10	0.0028	0.0058	0.0076
9.5	9.75	10	0.0053	0.00539	0.0107
15.1	12.3	10	0.0501	0.0487	0.0988
20.3	14.3	10	0.0956	0.0908	0.186
25.2	15.9	10	0.135	0.126	0.261
30	17.4	10	0.171	0.157	0.329
35.3	18.9	10	0.209	0.189	0.399
39.7	20.1	10	0.239	0.214	0.454
49.7	22.6	10	0.304	0.266	0.571
61.3	25.2	10	0.375	0.321	0.691

Table 12 The settings of the variables used in contact time optimization analysis

Variable name	C_0	S	L
Alias	Nil.	m	V
Unit	20 mg/L	g	L
Explanation	Original concentration	m, mass of the activated carbon	V, volume of the water
Value	(variable)	0.5	0.5

AC required in the two-stage operation by the following procedure.

A schematic flowsheet for a two-equilibrium-stage adsorption operation is shown in Fig. 1. The same amount of solution, L_s, is treated in each stage by different amounts of AC, S_{s1} and S_{s2}, in the two stages, respectively. The concentrations of the solution are reduced from C_0 to C_1 and C_1 to C_2, respectively.

The material balance for stage 1 is shown as follows:

$$L_s(C_0 - C_1) = S_{s1}\ (q_1 - q_0\ ) \tag{8}$$

And for stage 2, the material balance is as follows:

$$L_s(C_1 - C_2) = S_{s2}\ (q_2 - q_0\ ) \tag{9}$$

q_0 is the concentration of the adsorbate at the beginning stage and q_0 is always equal to zero as fresh activated carbon is used in each stage; q_1 and q_2 are the concentrations of the adsorbates of material leaving the stage 1 and 2, respectively.

According to equilibrium isotherm modelling, the Langmuir-Freundlich isotherm was selected to express the adsorption equilibrium based on the least SSE in the model application. This model was used to determine the minimum amount of activated carbon required for the two-stage process.

Table 13 Values of k_1, q_e, and n in pseudo-second kinetic model equation

C_0	k_1	q_e
10	0.00928	4.70
20	0.00981	7.33
30	0.00557	10.9
40	0.00510	13.2
50	0.00261	17.5
60	0.00207	21.1

The Langmuir-Freundlich isotherm is as follows:

$$q_e = \frac{q_m K_{lf} C_e^{\frac{1}{n_{lf}}}}{1 + K_{lf} C_e^{\frac{1}{n_{lf}}}} \tag{10}$$

The material balance for stage 1 became,

$$\frac{S_{s1}}{L_s} = \frac{C_0 - C_1}{q_1 - q_0} \tag{11}$$

$$\frac{S_{s1}}{L_s} = \frac{(C_0 - C_1)\left(1 + a_{LF} C_1^{n_{LF}}\right)}{K_{LF} C_1^{n_{LF}}} \tag{12}$$

and for stage 2, it becomes as follows:

$$\frac{S_{s2}}{L_s} = \frac{C_1 - C_2}{q_2 - q_0} \tag{13}$$

$$\frac{S_{s2}}{L_s} = \frac{(C_1 - C_2)\left(1 + a_{LF} C_2^{n_{LF}}\right)}{K_{LF} C_2^{n_{LF}}} \tag{14}$$

The total amount of adsorbent used was as follows:

$$\frac{S_{s1} + S_{s2}}{L_s} = \frac{1}{K_{LF}}\left(\frac{(C_0 - C_1)\left(1 + a_{LF} C_1^{n_{LF}}\right)}{C_1^{n_{LF}}} + \frac{(C_1 - C_2)\left(1 + a_{LF} C_2^{n_{LF}}\right)}{C_2^{n_{LF}}}\right). \tag{15}$$

$$\frac{d[(S_{s1} + S_{s2})/L_s]}{dC_1} \tag{16}$$

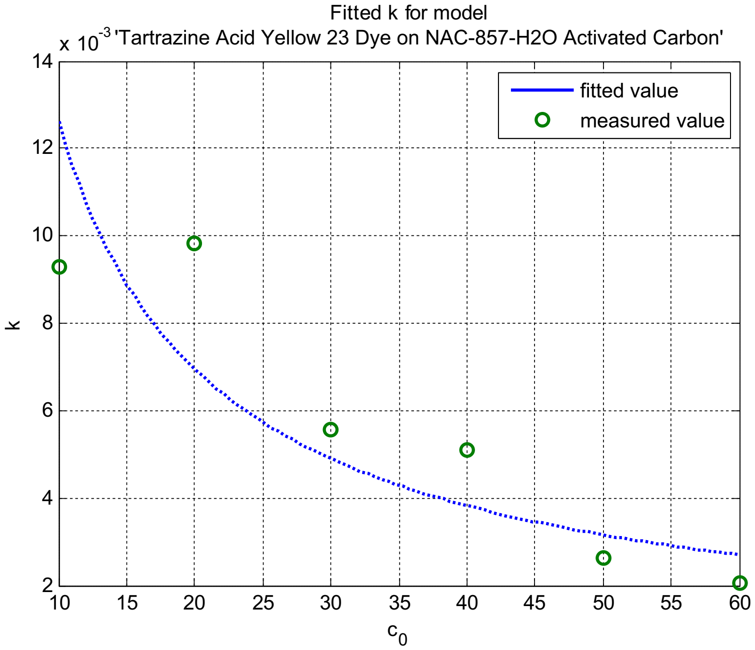
was set equal to zero in order to determine the minimum total adsorbent required. Thus, the equation becomes as follows:

$$\frac{1}{K_{LF}}\left[n_{LF}\frac{1}{C_1^{n_{LF}}}\left(\frac{C_0}{C_1} + 1\right) + \frac{1}{C_1^{n_{LF}}}\right] = \frac{1}{K_{LF} C_2^{n_{LF}}} \tag{17}$$

$$\text{Let}\, X = \left(\frac{C_1}{C_2}\right)^{b_F} - b_F\frac{C_0}{C_1} - 1 + b_F. \tag{18}$$

The intermediate concentration, C_1, was determined by setting the value of X in Eq. (18) to be zero using the

Fig. 3 Curve of *k* value versus C_0



solver add-in with Microsoft Excel spreadsheet. Thus, the amount of adsorbent required for each stage could be determined by Eqs. (12) and (13).

The required amounts of adsorbent to reduce the final effluent concentration to 1, 5 and 10% of the original concentration and 0.5, 1, 2, 5 and 10 ppm were investigated, respectively.

3 Results and Discussion

As a result of the carbonisation/activation process of pecan nut shells, an activated carbon was obtained and the material was designates NAC-857-H$_2$O; this material was used in all the equilibrium and isotherm studies.

Fig. 4 Curve of q_e value versus C_0

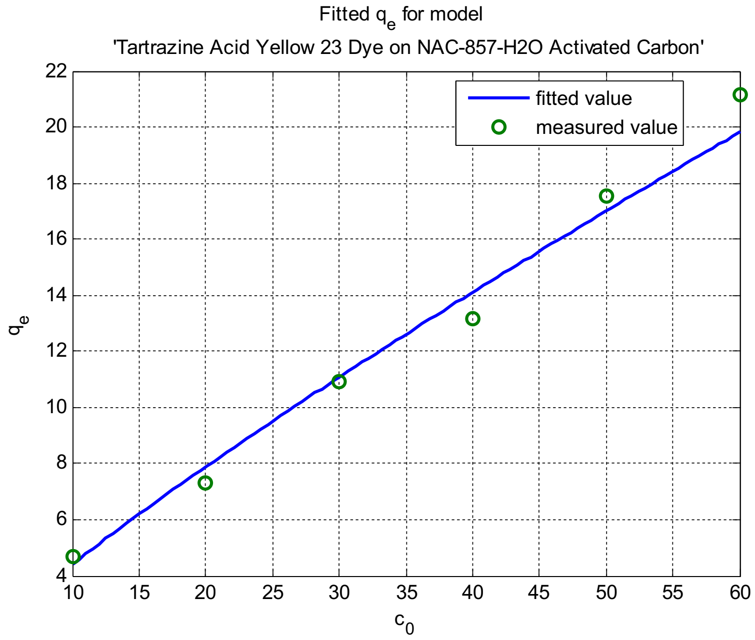
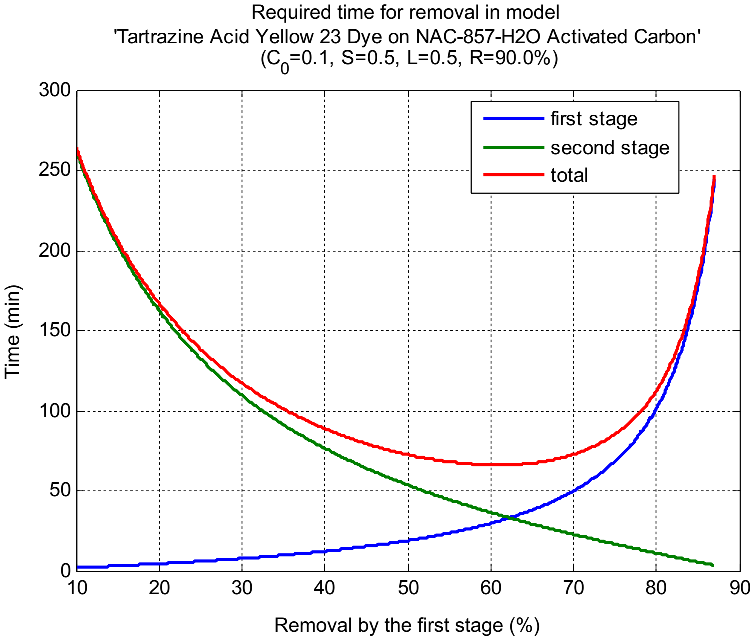


Fig. 5 Time optimization for tartrazine acid yellow 23 dye with 90% removal ($C_0 = 0.1$ mg/L)



3.1 Equilibrium Studies

The isotherm constants have been determined and the fitting results of equilibrium isotherm models of the azo dye (Tartrazine) are as shown in Table 3. The SSE values were obtained using Microsoft Solver.

As can be seen from Table 3, the SSE values of Freundlich and Langmuir-Freundlich isotherms were the lowest which means they are the best fitting models. This result can also be seen clearly from Fig. 2 where the curve of Langmuir-Freundlich isotherm fits best with the plots of the experimental data.

Fig. 6 Time optimization for tartrazine acid yellow 23 dye with 95% removal ($C_0 = 0.1$ mg/L)

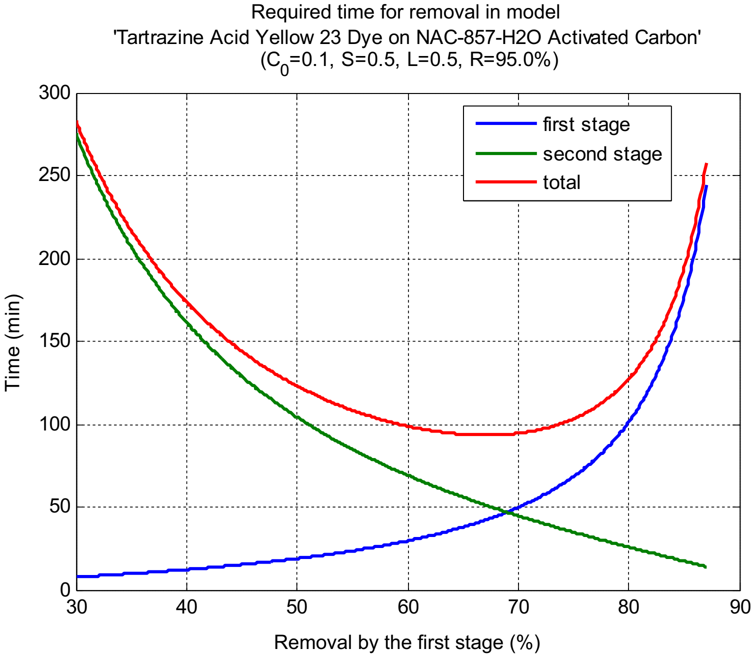
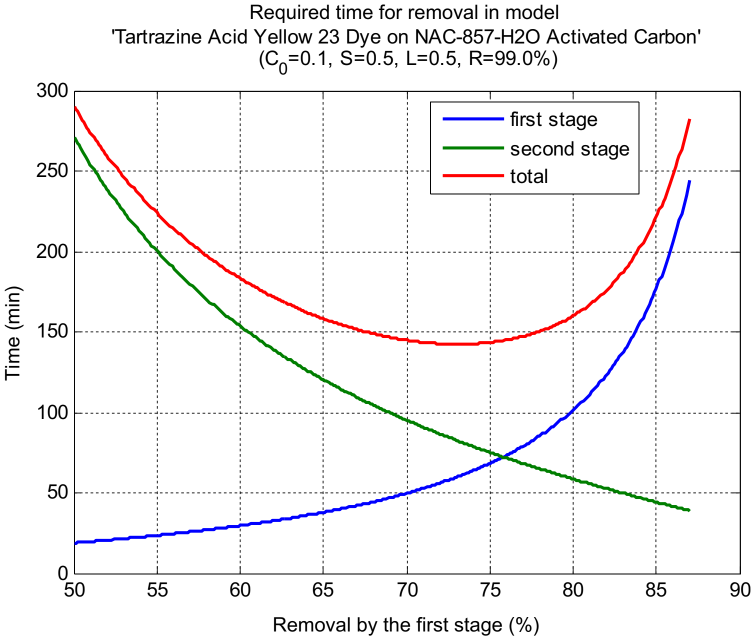


Fig. 7 Time optimization for tartrazine acid yellow 23 dye with 99% removal



Thus, Langmuir-Freundlich isotherm was used for the mass optimization. The intermediate concentration, C_1, was determined by setting the value of X in Eq. (18) to be zero using the solver add-in with Microsoft Excel Spreadsheet. Thus, the amount of adsorbent required for each stage could be determined by Eqs. (12) and (13).

The required amount of activated carbon to reduce the final effluent concentration to 1, 5 and 10% of the original concentration and 0.5, 1, 2, 5 and 10 ppm were investigated, respectively. Tables 4, 5, 6, 7, 8, 9, 10, and 11 show the summary of the optimised amounts of the required activated carbon

Fig. 8 Comparison of contact time needed for different percentage of removal (C_0 = 0.1 mg/L)

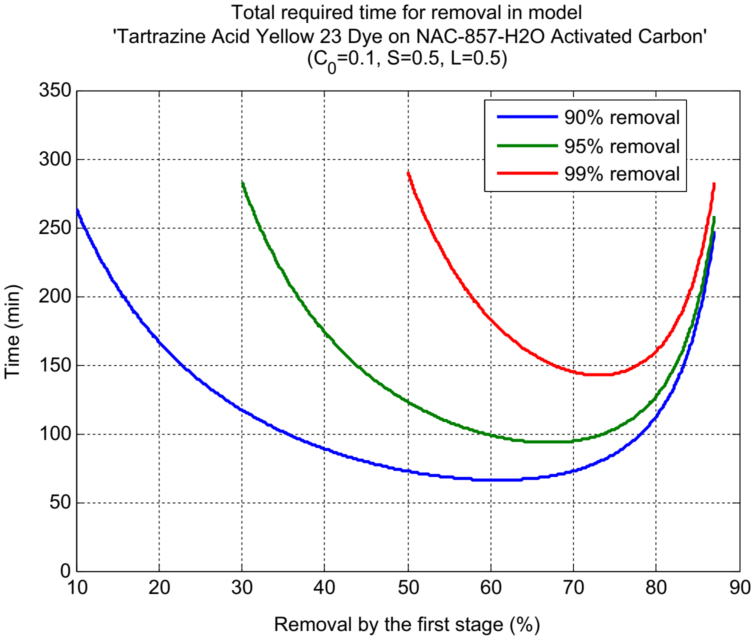
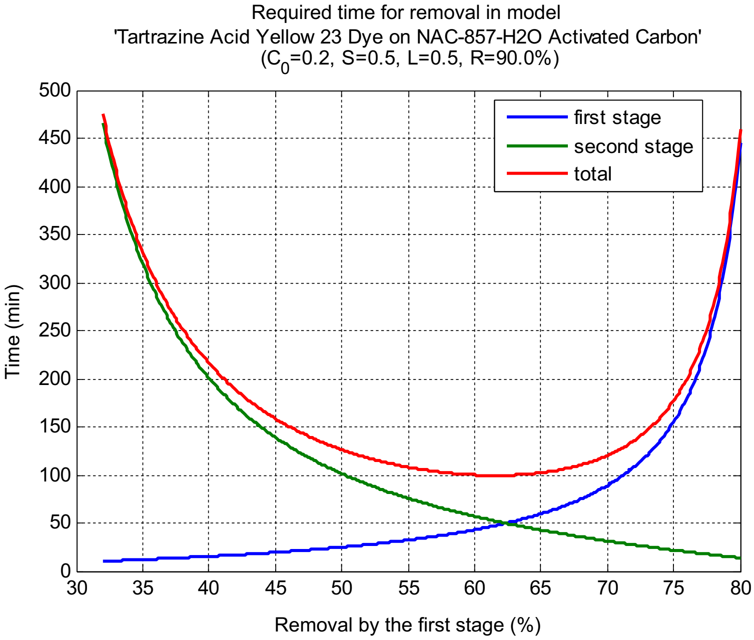


Fig. 9 Time optimization for tartrazine dye with 90% removal ($C_0 = 0.2$ mg/L)



obtained from pecan nut shells for different initial dye concentrations.

From the Tables 4, 5, 6, 7, 8, 9, 10, and 11, it can be inferred that the total amount of activated carbon needed for the adsorption increases as the value of C_0 increases and they are in a proportional relationship. C_1 also has a linear relationship with C_0. It was also observed that more adsorbent is required in the first stage than in the second stage. This is because the decrease in concentration is much larger in first stage than in second stage.

For the kinetic studies and contact time optimization of tartrazine acid yellow 23 dye on NAC-857-H2O

Fig. 10 Time optimization for tartrazine acid yellow 23 dye with 95% removal ($C_0 = 0.2$ mg/L)

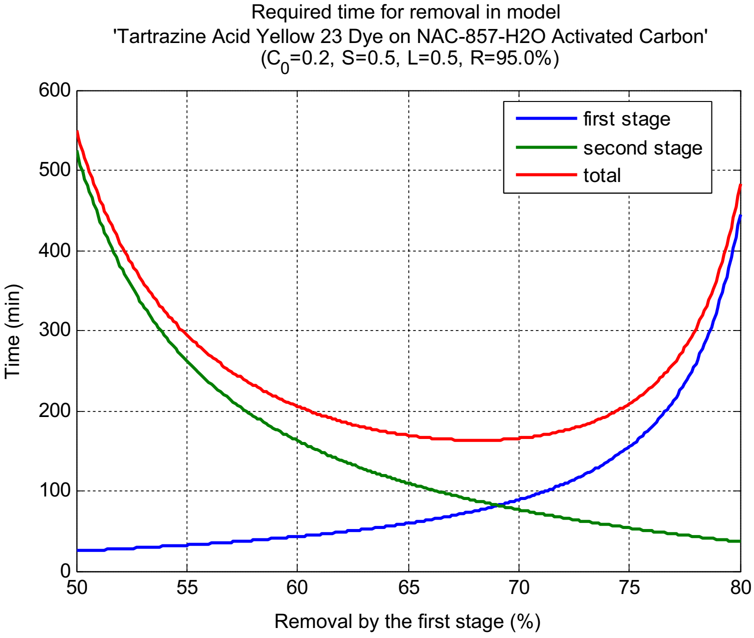
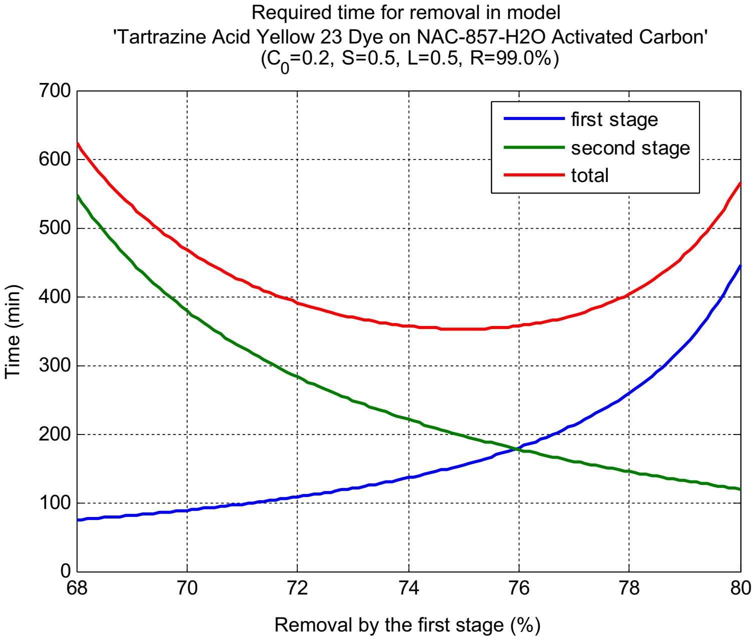


Fig. 11 Time optimization for tartrazine dye with 99% removal ($C_0 = 0.2$ mg/L)



Activated Carbon, the settings used for the analysis are shown in Table 12. The pseudo-second order model was employed to determine the contact time optimization as it had a good correlation with experimental data as shown in Table 13.

The parameter fit for the pseudo-second order model was describing by using the next equations

$$q_t = \frac{q_e^2 kt}{1 + q_e kt} \tag{19}$$

in which the parameters k and q_e are fitted by

$$\begin{cases} k = A_k c_0^{B_k} \\ q_e = A_{qe} c_0^{B_{qe}} \end{cases}, \tag{20}$$

and the fitted values parameters were 0.0917, −0.8611, 0.6397 and 0.8385 for A_k, B_k, A_qe and B_qe, respectively (Figs. 3 and 4).

For the determination of the optimization time for the pseudo-second order model, from the second order model Eq. (21):

$$q_t = \frac{q_e^2 kt}{1 + q_e kt} \tag{21}$$

The minimum time required to achieve an adsorption of q_t can be derived as follows

$$t = \frac{1}{kq_\mathrm{e}^2 (1/q_\mathrm{t} - 1/q_\mathrm{e})} = \frac{q_\mathrm{t}}{kq_\mathrm{e}(q_\mathrm{e} - q_\mathrm{t})} \tag{22}$$

where,

(a) $C_0 = 0.1$ mg/L, $S = 0.5$ g, $L = 0.5$ L, $R = 90\%$ (Fig. 5)

(b) $C_0 = 0.1$ mg/L, $S = 0.5$ g, $L = 0.5$ L, $R = 95\%$ (Fig. 6)

(c) $C_0 = 0.1$ mg/L, $S = 0.5$ g, L = 0.5 L, $R = 99\%$ (Fig. 7)

(d) ($C_0 = 0.1$ mg/L)(d) $C_0 = 0.1$ mg/L, $S = 0.5$ g, $L = 0.5$ L, comparison (Fig. 8)

(e) $C_0 = 0.2$ mg/L, $S = 0.5$ g, $L = 0.5$ L, $R = 90\%$ (Fig. 9)

(f) $C_0 = 0.2$ mg/L, $S = 0.5$ g, $L = 0.5$ L, $R = 95\%$ (Fig. 10)

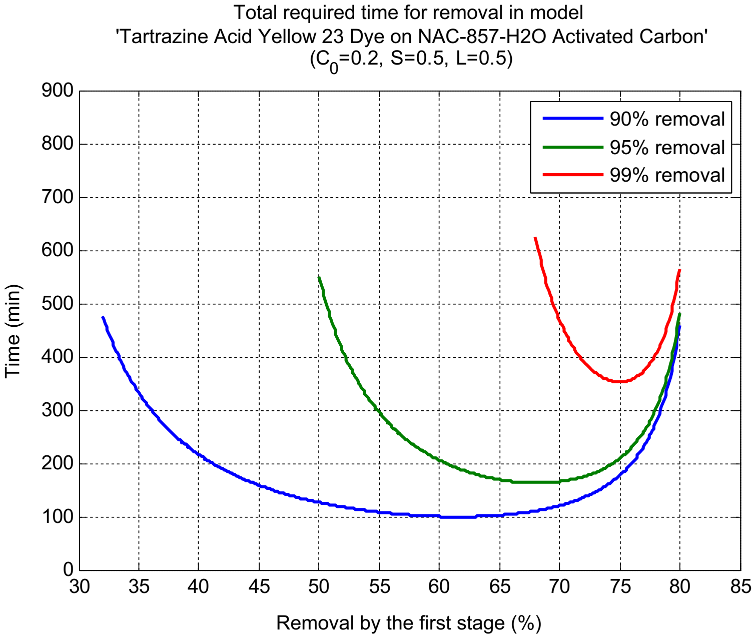


Fig. 12 Comparison of contact time needed for different percentage of removal (C_0 = 0.2 mg/L)

(g) $C_0 = 0.2$ mg/L, $S = 0.5$ g, $L = 0.5$ L, $R = 99\%$ (Fig. 11)

(h) $C_0 = 0.2$ mg/L, $S = 0.5$ g, $L = 0.5$ L, comparison (Fig. 12)

Figures 5, 6, 7, 8, 9, 10 and 11 show the two individual adsorption curves for the removal of tartrazine acid yellow 23 and the third curve is the resultant of the two-stage batch adsorber demonstrating the significant reduction in contact time that can be achieved. Figure 12 shows the contact time minimization curves for an initial tartrazine concentration of 0.2 mg/L to achieve three different percentage removals, namely, 90, 95 and 99%. The results show that the contact time is much lower for larger amounts of activated carbon used and lower initial tartrazine dye concentration. This is because more active sites were provided to take place when more activated carbon was used; therefore, a shorter contact time was needed. The condition was similar for low initial dye concentration. There was a significant difference between the number of sites and the number of dye molecules, so a shorter contact time was needed.

Obviously, for a higher percentage of dye removal or higher initial dye concentration, a longer contact time was required. To solve this problem, more carbon can be used so that more active sites were provided for the reaction. Therefore, the contact time can be reduced. If the amount of carbonaceous material was too small, a higher fractional dye removal may never be reached. Since the rate of the azo dye removal process was rapid initially, the activated carbon had already reached equilibrium with the dye molecules and it was unable to continue the process; therefore, the dye to activated carbon ratio must be considered in order to achieve a higher percentage of removal.

Usually, the contact time for stage 1 was shorter than that for stage 2. This is because the rate of the process was much faster in stage 1 since the dye concentration was very high initially. The activated carbon from pecan nut shells in stage 1 reached equilibrium quickly. In stage 2, the dye concentration has been already reduced; the rate of adsorption was limited by the amount of dye remained in the solution, which is much lower than in stage 1. Hence, a longer contact time was needed.

4 Conclusion

For the adsorption of tartrazine dye on the pecan shell derived activated carbon, the Langmuir-Freundlich equilibrium isotherm model provides the best fit with the experimental data. The total amount of activated carbon needed for the adsorption increased as the value of C_0 goes up and these two parameters exhibit a linear relationship. It was also observed that more adsorbent material is required in the first stage than in the second stage. This is because the decrease in concentration is much larger in first stage than in the second stage.

The contact time is much lower for larger amounts of activated carbon being used and for lower initial concentrations of the adsorbate. This is because more active sites were provided for adsorption to take place when more adsorbent was used. It was much easier for the adsorbate to attach onto the sites for exchange. As a result, a shorter contact time was needed. The condition was similar for low initial adsorbate concentrations.

For the two-stage batch adsorber analysis, usually, the contact time for stage 1 was shorter than that for stage 2. This is because the rate of the process was much faster in stage 1 since the adsorbate concentration was very high initially. The adsorbent in stage 1 reached equilibrium quickly. In stage 2, the adsorbate concentration had been already reduced; the rate of ion exchange process was limited by the amount of adsorbate ions remained in the solution. Hence, a longer contact time was needed. By varying the pecan derived carbon masses in each of the two stages the minimum total mass of carbon can be determined.

The minimum total contact time for a given set of parameters can be obtained by minimization of the kinetic rate equations.

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