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Equilibrium and Kinetic Modelling of Astrazon Yellow Adsorption by Sawdust: Effect of Important Parameters*

Naima Ouazene and Mohamed Nasser Sahmoune

Abstract

This paper aims to investigate the sorption of Astrazon yellow (A.Y.) onto sawdust (Aleppo pine tree), a forest waste as that acts as a low-cost adsorbent. In our experiments, the batch sorption is studied with respect to solute concentration, contact time, adsorbent dose, particle size and pH. The adsorption process attains equilibrium within 300 minutes. The extent of dye removal decreased with increasing particle size and increased with increasing contact time, adsorbent dose and pH. The equilibrium data were analysed by the Langmuir and Freundlich isotherms. The characteristic parameters for each isotherm were determined. By considering the experimental results and adsorption models applied in this study, it can be concluded that equilibrium data were represented well by the Langmuir isotherm equation. Maximum adsorption capacity calculated at 293K was 81.8 mg/g. Five kinetic models (pseudo-first order, pseudo-second order, fractional power, Elovich and intraparticle diffusion kinetic equations) were used to predict the adsorption rate constants. The kinetics of adsorption of the basic dye followed both Elovich and pseudo-second order kinetics, and intraparticle diffusion was not the sole rate-controlling step. The effective diffusion of Astrazon yellow in sawdust according to Boyd Model was $24.22\ .10^{-12}$ m^2/S. In order to reveal the adsorption characteristic of sawdust samples, SEM and FTIR spectra analyses were carried out. The results show that sawdust (Aleppo pine tree) can be an alternative low-cost adsorbent for removing cationic dyes from wastewater.

KEYWORDS: Astrazon yellow, sawdust, adsorption isotherm, low-cost adsorbents, kinetics

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1. INTRODUCTION

Dyes are discharged from various industries such as textile finishing, printing, dyestuff manufacturing and dyeing. Colour is the first contaminant to be recognised because it is visible to human eye. For some dyes, the dye concentration of less than 1 ppm in receiving water bodies is highly visible, so that even small quantities of dyes can colour large water bodies. In fact, effluents discharged from dyeing industries are highly coloured (Gupta and Suhas, 2009). It may be mutagenic and carcinogenic and can cause severe damage to human beings, such as dysfunction of the kidneys, reproductive system, liver, brain and central nervous system (Benguella and. Yacouta-Nour, 2009).

The treatment of dyes in textiles wastewaters pose several problems as they have complex aromatic structures which provide them with thermal, physico-chemical and optical stability. Due to their chemical structure, dyes are resistant to many chemicals, oxidizing agents and heat. They are biologically non degradable and therefore difficult to decolorize once released into aquatic environment (Do˘gan el al., 2007).

Possible methods of dye removal from textile effluents include, activates carbon, flotation, ion exchange, coagulation, biosorption, filtration, electrochemical treatments, precipitation and adsorption are the conventional methods for the removal colours from aqueous solutions. The advantages and disadvantages of each method have extensively reviewed (Gupta and Suhas, 2009; Crini, 2006).

Adsorption methods in solution systems play a vital role in many areas of practical environmental technology , which are mainly in wastewater treatment, because of several advantages such as high efficiency, simple operation and easy recovery/ reuse of adsorbent (Gupta and Suhas, 2009).

It has been reported that many types of adsorbent materials are effective in the removal of colour from aqueous solution. Activated carbon is extensively used as adsorbent due its high degree of effectiveness. However, it is quite expensive and also has high running costs (Crini, 2006; Rozada el al., 2003; Kanan and Sundaram, 2001)

In recent years, research is currently focusing on the use of low cost commercially available. Lignocellulosic waste materials as viable substitutes for activated carbon; in fact, wood sawdust and agricultural residues, relatively abundant and inexpensive materials, have been extensively investigated as adsorbents for removing contaminants from water (Batzias and Sidiras, 2007).

Many lignocellulosic waste materials, such as wood chips, peat, wheat straw, corncobs, barley husk and apple pomace have been successfully used to adsorb individual dyes and dye mixtures in textile effluent (Ferrero, 2007).

Among the lignocellulosic materials that have been investigated, sawdust is commonly used as adsorbent, especially for basic dyes, with capacity varying according to the structure of the dye and the mesh size (Batzias and Sidiras, 2007). Also, previously, some researchers have proved the success of several low-cost materials such as Apricot stone (Demirbas et al., 2008), wheat bran (Sulak et al., 2007) and Sepiolite (Tekbaş et al., 2009) for the removal of Astrazon yellow from aqueous solutions.

The present paper investigates the potential of abundantly available waste of sawdust (Aleppo Pine-tree) biomass as adsorbent for removal of the basic dye from synthetic aqueous solutions. Astrazon yellow was selected as a model compound in order to evaluate the capacity of sawdust for the removal of dyes from aqueous solutions.

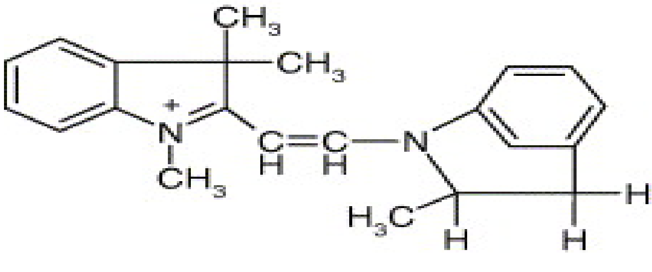
The effects of various factors including pH, adsorbent dosage, particle size, contact time and initial dye concentration on the adsorption were studied. To understand the nature of the adsorption, five sorption kinetic models (Pseudo-first order, Pseudo second order, Fractional power, Elovich, Intraparticle diffusion) were tested and both Langmuir and Freundlich isotherms were used to describe observed sorption phenomena.

2. MATERIALS AND METHODS

2.1 Materials

Astrazon Yellow 7 GLL (Scheme 1), (Molecular Formula $C_{20}H_{25}N_2$, Molecular Weight =293 g/mol, Color Index: Basic Yellow 21, λ_{max} = 416 nm (measured value)) was obtained from Dystar and used as received. Stock solution was prepared by dissolving accurately weighed dye in double distilled water. Experimental solutions of the desired concentrations were obtained by diluting the stock solution using distilled water.

Sawdust (Aleppo Pine-tree) procured from local timber industry was washed with tap water, air dried and used as such without any pretreatment to avoid extra expenditure.



Scheme 1: Astrazon Yellow 7 GLL

2.2 Determination of pHpzc

The zero point of charge $\left(pH_{pzc}\right)$ of sawdust was determined using a procedure similar to one described previously (Cerović et al., 2007): 20 ml of 0.01 mol/l KNO_3 solutions were placed in different closed conical flasks. The pH of each solution in each flask was adjusted to a value between 2 and 12 by adding HCl or NaOH solution. Then, 0.1 g of sawdust was added and the final pH measured after 24 h under agitation at room temperature. The pHpzc is the point where the curve of final pH versus initial pH crosses the line at final pH = initial pH.

2.3 Batch sorption experiments

The adsorption experiments were carried out by batch sorption method with the influence of solution pH, adsorbent dosage, particle size and initial dye concentration. Adsorption was performed by agitating a given dose of the adsorbent with 30 ml of sawdust dye solution of desired concentration at 20ºC in different shaker flasks in a thermostat shaker. The shaking speed was maintained at 200 rpm throughout the study. At the end of present time intervals, the sorbent was centrifuged and the concentration of dye solution was determined using UV-spectrometer. All experiments were carried out twice and the adsorbed dye concentrations were presented by means the average values of the two experimental results. The effect of pH was observed by studying the adsorption of dye over the pH range of 2 to 9. The pH of dye solution was adjusted with NaOH and HCl solution. The amount of sorption at time (t) and q_t (mg/g) was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

Where, C_0 (mg/l) is the initial dye concentration, C_t (mg/l) is the liquid phase concentrations of dye at any time, V is the volume of the solution (l) and m is the mass of dry adsorbent used (g). The amount of dye adsorbed at equilibrium, q_e (mg /g) was calculated by:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

Where C_e (mg/l) is the liquid phase concentrations of dye at equilibrium.

The dye removal percentage can be calculated as follows

$$R(\%)_t = \frac{(C_0 - C_t)}{C_0} * 100 \tag{3}$$

Due to the inherent bias resulting from linearization of the isotherm model and kinetic model, the non-linear regression Root Mean Square Error (RMSE) test was employed as criterion for the quality of fitting (Sahmoune et al, 2008). The root mean square error of a model is evaluated by:

$$RMSE = \sqrt{\frac{1}{n-2}\sum_{1}^{n}(q_i - q_{ie})^2} \tag{4}$$

Where, q_i (mg/g) is the experimental value of uptake, q_{ie} is the calculated value of uptake using a model (mg/g), and n is the number of observations in the experiment. The smaller RMSE value indicates the better curve fitting (Sahmoune et al, 2009).

3. RESULTS AND DISCUSSION

3.1 Effect of initial dye concentration and contact time

Equilibration time is an important parameter for economical wastewater treatment. The effects of contact time and initial dye concentration on Astrazon Yellow removal are shown in Figure1. The removal of Astrazon Yellow was rapid in the first 15-90 min, and gradually decreased with lapse of time until equilibrium. The rapid adsorption observed during the first 90 min is probably due to the abundant availability of active sites on the sawdust surface, and with the gradual occupancy of these sites, the sorption becomes less efficient. At this point, the amount of Astrazon Yellow being adsorbed onto the adsorbent was in state of dynamic equilibrium with the amount of dye desorbed from the adsorbent. The time required to attain this state of equilibrium was termed as the equilibrium time and the amount of dye adsorbed at the equilibrium reflect the maximum dye adsorption capacity of the adsorbent under these particular conditions (Do˘gan el al., 2009).

It is clear from figure 1 that the contact time needed to reach equilibrium conditions was about 300 min. In line with these results, the agitation time was fixed at 300 min (5h) for the rest of the batch experiments to make sure that full equilibrium was reached. It also shows that the amount of Astrazon Yellow adsorbed increased with an increase in initial Astrazon Yellow concentration. This is due to increase in driving force of the concentration gradient with increasing initial dye concentration: increasing initial dye concentration increases the number of collisions between dye cations and sorbent, which enhances the sorption process (Jain and Shrisvastava; 2008). In addition, a higher initial concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases, thus increases the uptake. A similar trend was reported for the adsorption of dyes such as Malachite Green onto Perlite (Govindasamy et al., 2009), Maxilon Yellow on Kaolinite (Do˘gan el al., 2009), Methylene Blue on Pineaple Stem (Hameed et al; 2009) and Methylene Blue on Bioenergy Forest Waste (Yao et al., 2009).

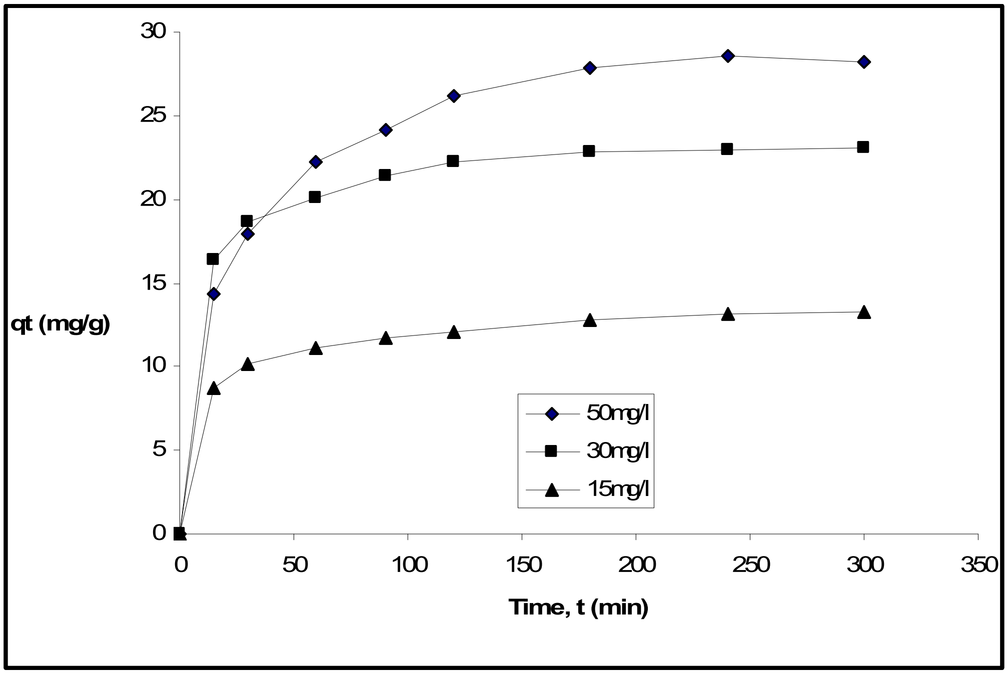


Figure 1. Effect of initial dye concentration and contact time on the adsorption of A.Y onto sawdust (adsorbent dosage: 0.67 g/l, particle size; <1.6 mm, T°=: 293 K).

3.2 Effect of adsorbent dosage

Adsorbent dosage is an important parameter because this factor determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The adsorption performance of the adsorbent was tested by using different amounts of sorbent and these results are presented in Figure 2. This figure shows that the amount of dye adsorbed increases rapidly with adsorbant dosage in the beginning and very slowly towards the end of the reaction. AY removal efficiency increased from 30 to 91 % with increasing dosage from 0.33 to 4. g/l and then remained almost constant. This was caused by the fact that with increasing adsorbent dosage more adsorption sites are available (Hameed et al; 2009). However, increasing the sites had little effect on removal efficiency at high adsorbent dosage because of the establishment of equilibrium at extremely low adsorbate concentration in the solution before reaching saturation adsorption (Yao et al., 2009, Bulut and Aydin, 2006).This experiment also indicated that AY required higher adsorbent doses for yielding 100% removals. Similar findings have also reported by other researchers (Hameed et al; 2009, Akkaya and Ozer, 2005, Gupta et al., 2006).

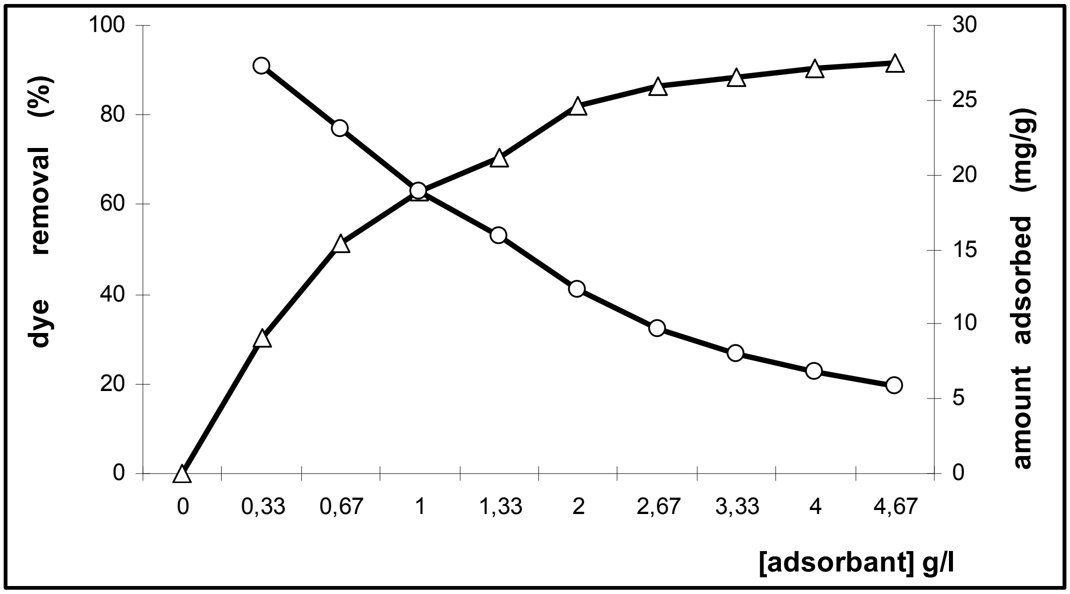


Figure 2. Effect of adsorbent dosage on the adsorption of A.Y onto sawdust (dye concentration: 30 mg/l, particle size: < 1.6 mm, temperature: 293 K, contact time: 5 h).

3.3 Effect of particle size

Another parameter studied for the uptake of Astrazon Yellow was the influence of the particle size of the sawdust biomass. The adsorption studies were carried out at nine different particle sizes at fixed adsorption dose (0.67 g/l), contact time 5 h, adsorbate concentration 30 mg/L and temperature 293 K. The selected particle sizes were < 0.08, 0.08-0.1, 0.1-0.25, 0.25-0.315, 0.315-0.4, 0.45-0.5, 0.5-0.63, 0.63-1, 1-1.6 particle size. It was observed (see figure3) that as the particle size decreases; the adsorption of the dye increases and hence the removal of the dye increases. This is due to larger surface area that is associated with smaller particles. For larger particles; the diffusion resistance to mass transport is higher and most of the internal surface of the particle may not be utilised for adsorption and consequently; the amount of dye adsorbed is small (Jain and Shrisvastava; 2008). Whereas the breaking of large particle tend to open tiny cracks and channels on the particle surface, providing added surface area (for small particles) removes more dye in the initial stages of the adsorption process than the large particles (Khattri and Singh; 2000). Maximum adsorption about 70 % could be achieved at the particle size < 0.08 mm. similar observation has been reported for the removal of Astrazon Yellow from aqueous solutions by adsorption onto wheat bran (Sulak et al., 2007).

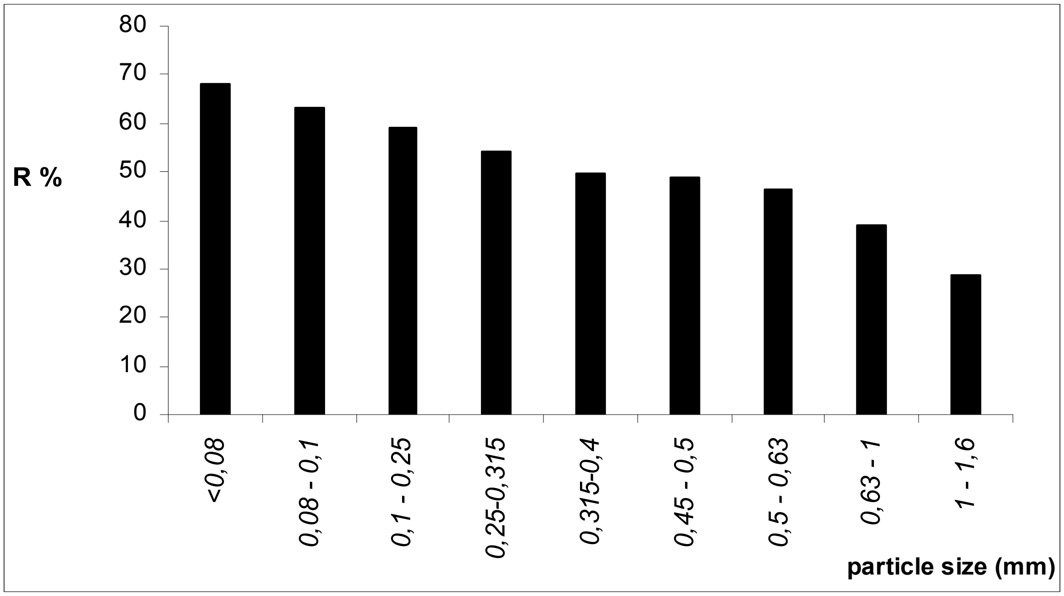


Figure 3. Effect of particle size on the adsorption of A.Y onto sawdust, (dye concentration: 30 mg/l, temperature: 293 K, adsorbent dosage: 0.67 g/l, contact time: 5 h).

The specific surface area is approximated as the external surface area. Moreover the particles are supposed spherical and S, calculated as the external surface compared to the solid/liquid ratio in the solution, gives

$$S = \frac{6m}{d_p \rho_{app}} \tag{5}$$

Where m is the adsorbent mass concentration in the solution (kg.m^{-3}), d_p is the particle size diameter (m) and ρ_{app} the apparent volume mass of the adsorbent (kg. m^{-3}).The physical properties of this adsorbent are shown in Table 1

Table 1. The physical characteristics of the biomass

Parameters	Results
Particle size d_p (μm)	<1600
Humidity (%)	9.362
Density	0.3055
Specific area (m $^{-1}$)	56.11

*An average value of d_p was used for calculation

3.4 Effect of pH

The pH of the dye solution plays an important role in the whole adsorption process, particularly on adsorption capacity (Do˘gan el al., 2008, Bulut and Aydin, 2006; Govindasamy et al., 2009). The adsorption behaviour of the dye on sawdust was studied over a wide pH range of 2–9. The effect of pH on the adsorption of A.Y is shown in figure 4. It is evident that the percentage colour removal of Astrazon Yellow increased consistently with pH. Several investigations have reported that A.Y adsorption usually increases as the pH is increased (Demirbas et al., 2008; Sulak et al., 2007). The increase in sorption depended on the properties of the adsorbent surface and the dye structure. This behaviour of dye sorption can be explained on the basis of surface charge of the adsorbents. The net charge on the adsorbent is pH-dependent because the adsorbent surface has biopolymers with many functional groups.

The effect of pH on adsorption by sawdust can be explained on the basis of the point of zero charge pHpzc, at which the adsorbent is neutral. The surface charge of the adsorbent is positive when the media pH is below the pHpzc value, while it is negative at a pH over the pHpzc (dulman et al., 2009). In the present work, the obtained value of pHzpc of sawdust is 6.8 as seen in figure 5, and over this pH, the surface charge of the adsorbent is negative. As the pH of the system increases, the number of positively charged sites decreases while the number of the negatively charged sites increases. The negatively charged sites favour the adsorption of dye cation due to electrostatic attraction.

Similar pHzpc values for various sawdust materials (polyacrylamide-grafted sawdust = 5.9, dyestuff-treated sawdust = 5.9, sawdust activated carbon = 6.4, rubber wood sawdust carbon = 5.8) were reported by other authors (Shukla et al., 2002). It appears from the results obtained in the present investigation that in

Similar pHzpc values for various sawdust materials (polyacrylamide-grafted sawdust = 5.9, dyestuff-treated sawdust = 5.9, sawdust activated carbon = 6.4, rubber wood sawdust carbon = 5.8) were reported by other authors (Shukla et al., 2002). It appears from the results obtained in the present investigation that in the alkaline medium the negatively charged species starts dominating and the surface tends to acquire a negative charge. As the adsorbent surface is negatively charged, the increasing electrostatic attraction between positively charged adsorbate species and negatively charged adsorbent particles would lead to increased adsorption of the dye. The results are in general agreement with other previous studies (Dulman and Cucu-Man, 2009; Batzias and Sidiras, 2007; Khatri and Singh, 2009.

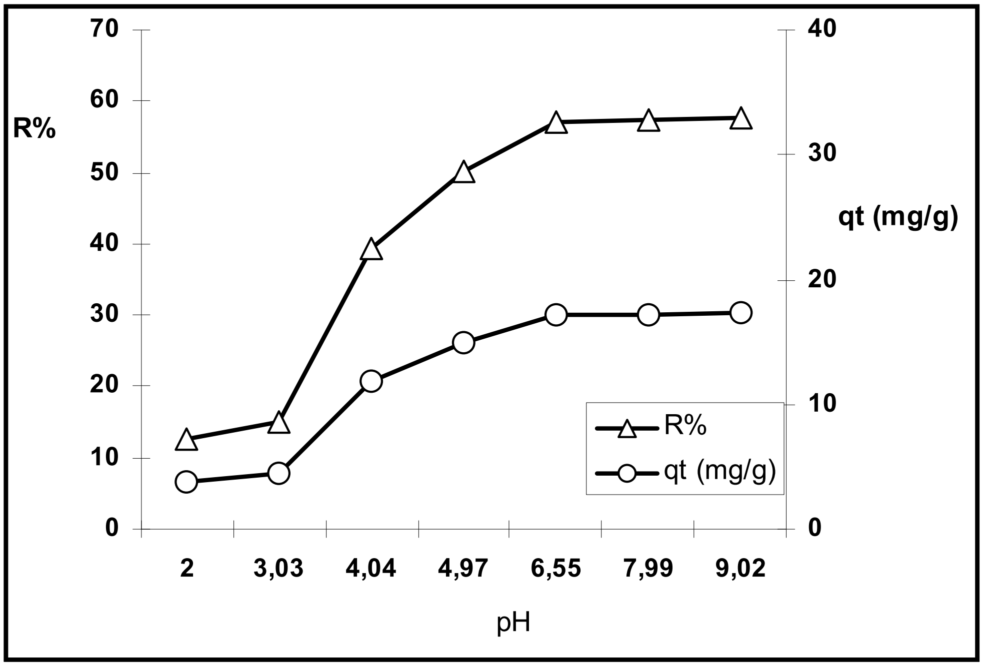


Figure 4. Effect of pH on the adsorption of A.Y on sawdust (dye concentration 30 mg/l, adsorbent dosage 1 g/l, particle size: < 1.6 mm , temperature:293K, contact time:300 min)

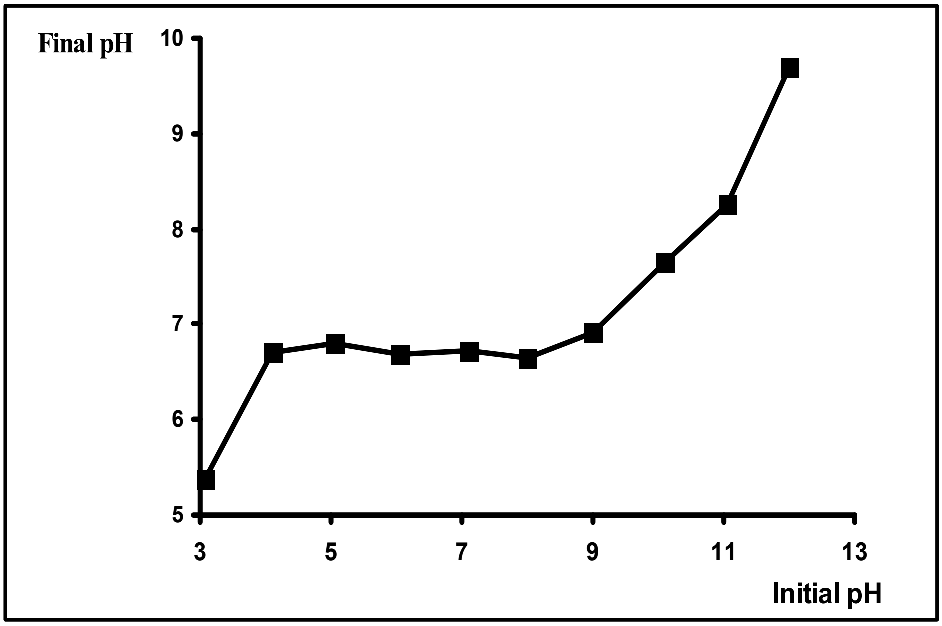


Figure 5. Zero point charge (pHzpc) of the used adsorbent for the adsorption experiment

3.5 Kinetics of adsorption

In order to examine the mechanism of adsorption process such as chemical reaction and mass transfer, a suitable kinetic model is needed to analyze the rate data. Many models such as pore diffusion model, homogeneous surface diffusion model, and heterogeneous diffusion model (also known as pore and diffusion model) have been extensively applied in batch reactors to describe the transport of adsorbates inside the adsorbent particles (O¨ rnek et al., 2007;Wu el al.,2001). Any kinetic or mass transfer representation is likely to be global. From a system design viewpoint, a lumped analysis of kinetic data is hence sufficient for practical operations.

3.5.1. Pseudo first-order equation

The sorption kinetics may be described by a pseudo first-order equation (Sahmoune et al, 2009: Ho and Chiang, 2001). The linear pseudo first-order equation is the following:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (6)$$

Where q_e and q_t are the amounts of dye adsorbed at equilibrium and at time t (mg/g), respectively, and k_1 is the equilibrium rate constant of pseudo first-order adsorption, (1/min).

The slopes and intercepts of plots of $\log(q_e - q_t)$ versus t were used to determine the first-order rate constant k_1 and the amount of dye sorbed at equilibrium q_e. However, the experimental data deviated considerably from the theoretical data. A comparison of the results with the correlation coefficients is shown in Table 2. The Root Mean Square Error for the first-order kinetic model obtained at all the studied concentrations were high. Also the theoretical q_e values found from the first-order kinetic model did not give reasonable values. This suggests that this adsorption system is not a first-order reaction.

3.5.2 Fractional power model

The adsorption kinetics can also be described by power function equation (Sahmoune et al, 2008). The linear power function equation is the following

$$\ln q_t = \ln k + \nu \ln t \tag{7}$$

The plot $\ln q_t$ and $\ln t$ should give linear relationship from which ν and k can be determined from the slope and intercept of the plot respectively. The rate constant of power function ν was found to be 0.1361. The results indicate that the power function model described the time-dependent Astrazon Yellow on sorbent as the value of constant ν was less than 1 (Basha and Murthy, 2007). The kinetic of Astrazon Yellow adsorption can be satisfactory described by power function model. Power model describes rates of adsorption (as in the common Freundlich model) and chemical reaction (for estimation of reaction orders). However, the regression coefficient R^2 is not very high (<0.98) which indicate that power function is not the best model to correlate kinetic data.

3.5.3 Pseudo second-order equation

The adsorption kinetics may also be described by a pseudo second-order equation (Ho and McKay, 1998, Sahmoune et al, 2009)

The linear pseudo second-order equation is the following:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{8}$$

Where k_2 the equilibrium is rate constant of pseudo second-order adsorption (g/mg min).

The slopes and intercepts of plots t/q_t versus t were used to calculate the second-order rate constants k_2 and q_e . The straight lines in plot of t/q_t versus t show good agreement of experimental data with the second-order kinetic model for different initial dye concentrations. Table 2 lists the computed results obtained from the second-order kinetic model. The correlation coefficients for the second-order kinetic model obtained were greater than 0.991for all concentrations. The calculated q_e values also agree very well with the experimental data. These indicate that the adsorption system studied belongs to the second-order kinetic model.

3.5.4 Intraparticle diffusion equation

Because Equations. 6, 7 and 8 can not identify the diffusion mechanisms, the intraparticle diffusion model was also tested (Govindasamy et al., 2009; Dulman and Cucu-Man, 2009; Demirbas et al., 2008). The rate parameters for intraparticle diffusion (k_{int}) at different initial concentrations are determined using the following equation.

$$q_t = k_{\text{int}} t^{\frac{1}{2}} \tag{9}$$

Where k_{int} is the intraparticle diffusion rate constant, (mg/gmin$^{1/2}$)

Figure 6 show a plot of q_t vs.$t^{\frac{1}{2}}$ for the present system. The plot of q_t against $t^{\frac{1}{2}}$ may present a multi-linearity correlation, which indicates that two steps occur during adsorption process. The mechanism of adsorption is complex but that intraparticle diffusion is important in the early stages. In this case, the first linear portions in figure 6 could be due to intraparticle diffusion effects. The slopes of these linear portions can be defined as a rate parameter and characteristic of the rate of adsorption in the region where intraparticle diffusion is occurring. Initially, within a short-time period, it is postulated that the dye was transported to the external surface of the sawdust through film diffusion and its rate have been very fast. After saturation of the surface, the dye molecule entered into the sawdust by intraparticle diffusion through pore and interior surface diffusion until equilibrium is attained which is represented by the second straight lines in figure 6. Several previous investigations have reported a similar type of pattern (Eren, 2009; Hameed et al, 2009).

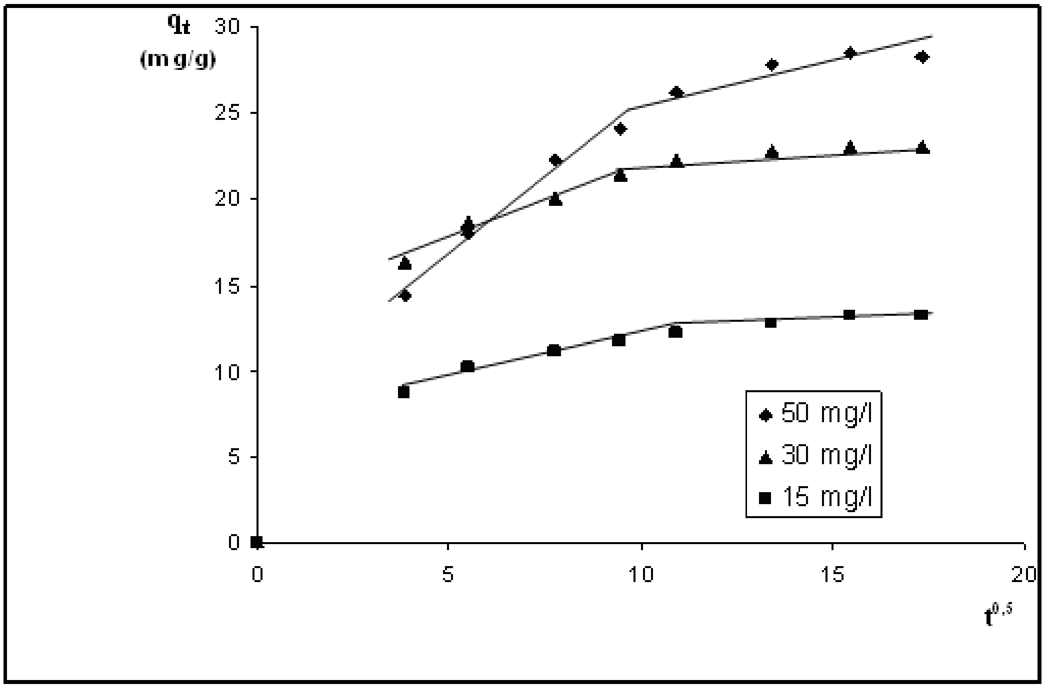


Figure 6. Amount of dye adsorbed q_t vs.$t^{\frac{1}{2}}$ for intraparticle diffusion of AY by sawdust sample at different initial dye concentrations, particle size: <1600 μm, T = 293 K, initial pH 7.50, and m= 0.67 g/l.

3.5.5 The Elovich equation

The linear Elovich equation is given as follows (O¨ rnek et al., 2007; Ho and McKay, 2000; Sahmoune et al, 2009).

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{10}$$

Where α is the initial sorption rate (mg/g min), and the parameter β is related to the extent of surface coverage and activation energy for chemisorption (g/mg).

In this case, a linear relationship was obtained between dye adsorbed, qt, and $\ln t$ over the whole adsorption period, with residual root mean square error between 01603 and 0.4817for all the lines (table 2). Also Table 2 lists the kinetic constants obtained from the Elovich equation. In the case of using the Elovich equation, the Root Mean Square Error (RMSE) are lower than those of the pseudo second-order equation, hence it may be used to describe the kinetics of adsorption of Astrazon Yellow onto sawdust.

The Elovich equation describes predominantly chemical adsorption on highly heterogeneous adsorbents, but the equation does not propose any definite mechanism for adsorbate–adsorbent interaction (Ho and McKay, 1998). Although the Elovich equation does not provide any mechanistic evidence, it has proved suitable for highly heterogeneous systems of which the adsorption of Astrazon Yellow onto sawdust is undoubtedly such a case.

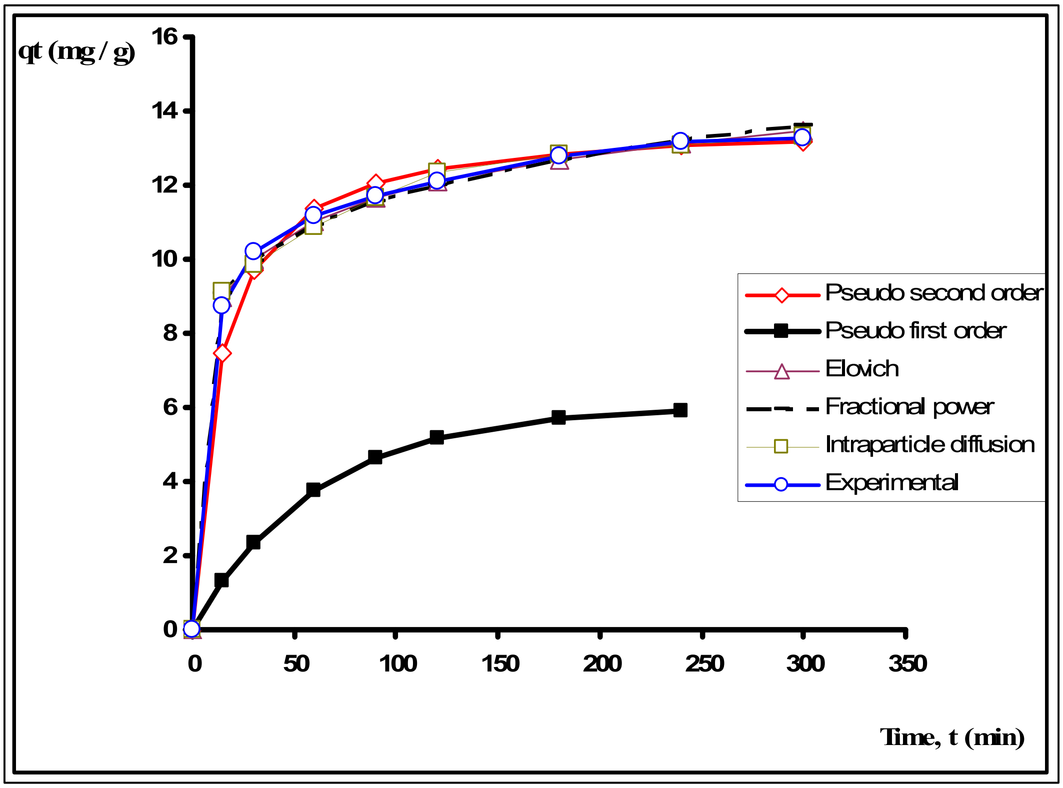


Figure 7. Comparison between the measured and modelled time profiles for adsorption of Astrazon Yellow (15 mg/l initial dye concentration) onto Sawdust.

A comparison of calculated and measured results for 15 mg/L initial dye concentration is shown in figure 7. As can be seen from figure 7, Elovich equation provides the best correlation for all of the sorption process, whereas the pseudo second-order equation and intraparticle diffusion also fits the experimental data well. The pseudo first-order does not give a good fit to the experimental data for the adsorption of Astrazon Yellow.

The adsorption systems studied belong to the second-order kinetic model, based on the assumption that the rate limiting step may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate. The agreement of the Elovich equation with experimental data may be explained as below. The previous successful application of the Elovich equation to heterogeneous catalyst surfaces helps to explain its success in predicting the sorption of metal complex dyes on sawdust. The general explanation for this form of kinetic law involves a variation of the energetics of chemisorption with the active sites are heterogenous sawdust and therefore, exhibit different activation energies for chemisorption (Özacar and Şengil, 2005).

Because the cell walls of sawdust mainly consist of cellulose and lignin, and many hydroxyl groups, such as tannins or other phenolic compounds (Özacar and Şengil, 2005).

Kinetic data could be treated by models given by Boyd et al (1947), because adsorption mechanism follows the intra-particle diffusion process (figure 6 and 7). From figure 6 the data points are related by two straight lines—the first straight portion depicting macropore diffusion and the second representing micro-pore diffusion (Srivastava et al., 2006). These show only the pore diffusion data. Extrapolation of the linear portions of the plots back to the *y*-axis gives the intercepts, which provide the measure of the boundary layer thickness. The deviation of straight lines from the origin (Figure 6) may be due to difference in rate of mass transfer in the initial and final stages of adsorption. Further, such deviation of straight line from the origin indicates that the pore diffusion is not the sole rate-controlling step. The adsorption data for q_t versus $t^{0.5}$ for the initial period show curvature, usually attributed to boundary layer diffusion effects or external mass transfer effects (Srivastava et al., 2006). The slope of the Weber and Morris plots – q_t *versus* $t^{0.5}$ – are defined as a rate parameter, characteristic of the rate of adsorption in the region where intra-particle diffusion is rate controlling For adsorption particles of spherical shape, the simplified Boyd equation is as follow:

$$\ln\left[\frac{1}{1-F^2(t)}\right]=\frac{\pi^2 D_i}{r_0^2}t \qquad (11)$$

$$\text{Where} \quad \mathrm{F}(\mathrm{t})=\frac{q_t}{q_e} \qquad (12)$$

$\mathrm{F}(\mathrm{t})$ is the fractional attainment of equilibrium at time *t*, D_i the effective diffusion coefficient of adsorbate in the adsorbent phase (m^2/s), r_0 the radius of the adsorbent particle assumed to be spherical (m). Thus the slope of the plot of $\ln\left[\frac{1}{1-F^2(t)}\right]$ versus *t* would give D_i .The calculated values of D_i is 24.22 .10^{-12} m^2/s. This shows that A.Y has highest overall pore diffusion rate. Due to this reason, the initial adsorption of A.Y on sawdust is highest in comparison to other dyes (Mall et al., 2006).

Table 2. Kinetic parameters for the adsorption of Astrazon Yellow on sawdust

Models	**Parameters**	**[AY]$_{\text{initial}}$ = 15 mg/l**	**[AY]$_{\text{initial}}$ = 30 mg/l**	**[AY]$_{\text{initial}}$ = 50 mg/l**
Pseudo-second-order	R^2	0.9993	0.9998	0.991
	k_2 (g.mg^{-1} min^{-1})	5.80 10^{-3}	4.90 10^{-3}	1, 66.10^{-3}
	q_e cal (mgg^{-1})	13.7363	23.7529	30.40
	q_e exp (mgg^{-1})	13.2441	23.0511	28.21
	h (mg.g^{-1}min^{-1})	1.096	2.764	1.53
	RMSE	0.5954	0.6149	0.734
Pseudo-first-order	R^2	0.9603	0.9933	0.9757
	k_1 (g.mg^{-1} min^{-1})	0.016	0.022	0.021
	q_e exp (mgg^{-1})	6.045	10.009	8.75
	RMSE	8.63	15.58	1.2086
Fractional power	R^2	0.9774	0.9525	0.9554
	k	6.26	12.24	8.1727
	v	0.1361	0.1149	0.2318
	RMSE	0.25	0.6033	1.39
Elovich	R^2	0.991	0.966	0.9766
	a_e ($mg.g^{-1}$ min^{-1})	39.34	245.70	6.7652
	β_e (g.mg^{-1})	0.6664	0.4372	0.2026
	RMSE	0.1603	0.4817	0.8570

3.6 Adsorption isotherms

Figure 8 shows the equilibrium adsorption isotherm of Astrazon Yellow by sawdust. The isotherm rises sharply in the initial stages for low *C*e and *q*e values. This indicates that there are plenty of readily accessible sites. Eventually a plateau is reached, indicating that the adsorbent is saturated at this level. The decrease in the curvature of the isotherm, tending to a monolayer, considerably increasing the *C*e values for a small increase in *q*e, is possibly due to the less active sites being available at the end of the adsorption process and/or the difficulty of the edge ions in penetrating the adsorbent, dye cations partially covering the surface sites.

The analysis and design of the adsorption process requires equilibrium to better understand the process. Sorption equilibria provide fundamental physicochemical data for evaluating the applicability of the sorption process as a unit operation. In the present investigation the equilibrium data were analysed using the Freundlich and Langmuir isotherm expression given by the following equations (Freundlich, 1906; Langmuir, 1916)

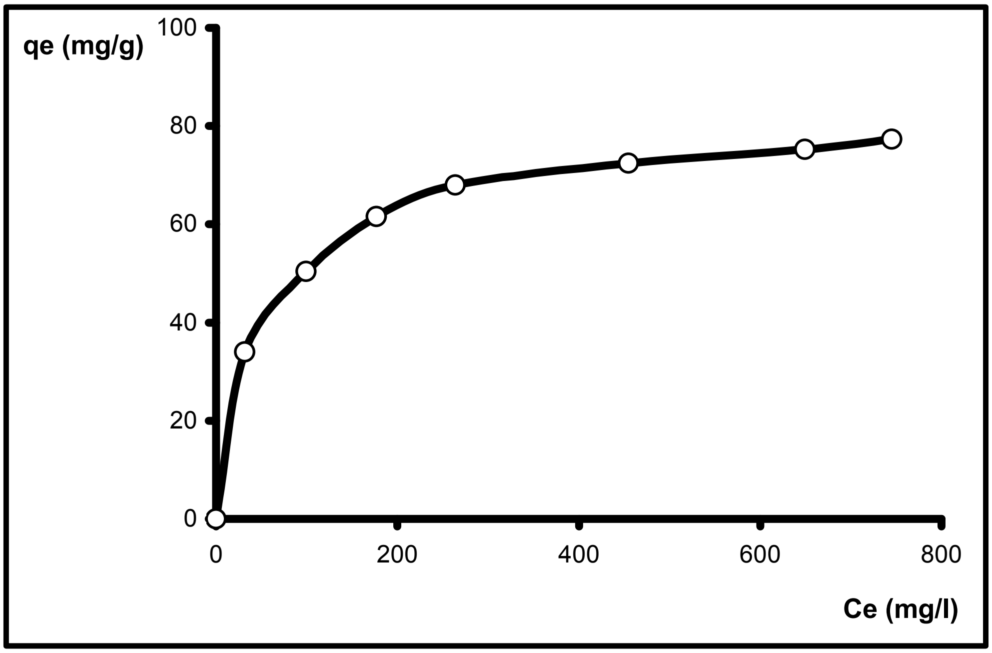


Figure 8. Equilibrium isotherm of AstrazonYellow on sawdust.Conditions: Adsorbent dosage: 2 g/l, particle size: < 1.6 mm, contact time: 300 min, temperature 293K and pH 7.5

Freundlich

$$q_e = K_f C_e^{\frac{1}{n}} \tag{13}$$

Where K_f and *n* are the Freundlich constants characteristic of the system.

Equation 13 can be linearized in a logarithmic form and the Freundlich constants can be determined

Langmuir

$$q_e = q_{\max} \frac{bC_e}{1 + bq_{\max}} \tag{14}$$

where $q_{\max}$ (mgg^{-1}) is the maximum amount of dye per unit weight of mixture to form a complete monolayer on the surface bound at high C_e, and *b* (lmg^{-1}) is a constant related to the affinity of the binding sites.

The linearized forms of the Freundlich and Langmuir isotherms are shown in Table 3. It was observed that the Langmuir isotherms could be linearized to at least four different types. Type 1 Langmuir isotherm was the most commonly used linear expression to study the relation between the concentration of solute in the liquid phase and in the solid phase at equilibrium conditions. Type 2 Langmuir expressions were also used to explain the equilibria phenomena of dye adsorption process.

Table 3. Isotherms and their linear forms

Isotherm	**Type**	**Linear form**	**Plot**
Freundlich	-	$\ln q_e = \ln K_f + (1/n)\ln C_e$	$\ln q_e vs. \ln C_e$
Langmuir	Type 1	$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{bq_{\max}}$	$\frac{C_e}{q_e}$ vs. C_e
	Type 2	$\frac{1}{q_e} = \frac{\left(\frac{1}{bq_{\max}}\right)1}{C_e} + \frac{1}{q_{\max}}$	$\frac{1}{q_e}$ vs. $\frac{1}{C_e}$
	Type 3	$q_e = q_{\max} - \frac{\left(\frac{1}{b}\right)q_e}{C_e}$	q_e vs. $\frac{q_e}{C_e}$
	Type 4	$\frac{1}{C_e} = \frac{bq_{\max}}{q_e} - b$	$\frac{1}{C_e}$ vs. $\frac{1}{q_e}$

The Langmuir constants $q_{\max}$ and b can be calculated from the plot between $\frac{C_e}{q_e}$ vs. $\mathrm{C_e}$, $\frac{1}{q_e}$ vs. $\frac{1}{\mathrm{C_e}}$, q_e vs. $\frac{\mathrm{q_e}}{\mathrm{C_e}}$ and $\frac{1}{C_e}$ vs. $\frac{1}{\mathrm{q_e}}$ for Type 1, 2, 3 and 4 Langmuir isotherms respectively. Similarly the Freundlich isotherm constants K_f and n can be calculated from the plot of $\ln q_e vs. \ln C_e$. The predicted isotherm constants and their corresponding error function RMSE values by linear method are shown in Table 4.

Table 4. Isotherm constant for Astrazon Yellow on sawdust

Models	**Langmuir**				**Freundlich**
Parameters	**Type1**	**Type2**	**Type3**	**Type4**	
RMSE	2.1820	2.72250	3.3441	2.6195	4.3544
R^2	0.9994	0.9843	0.962	0.9843	0.9514
qmax ($mg.g^{-1}$)	81.769	78.125	79.195	78.378	-
b ($l.mg^{-1}$)	0.0178	0.0234	0.02211	0.023	-
K_f (mg/g)					15.19
n					3.925

From Table 4, it can be observed that the calculated isotherm parameters and their corresponding RMSE values vary for the four linearized types (Types 1–4) of the Langmuir isotherm. The Langmuir isotherm was found to be the best-fitting isotherm; Type 1 Langmuir isotherm showed better fit followed by type 4 Langmuir isotherms**.**

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L which is defined by Hall and Vermeylem (1966) as

$$R_L = \frac{1}{1+bC_0} \tag{15}$$

Where b is the Langmuir constant and C_0 is the initial concentration of the adsorbate in solution. The values of RL indicate the type of isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$). The dimensionless separation factors calculated for Astrazon Yellow on sawdust is between 0.059 and 0.359. The R_L values are found to be less than 1 and greater than zero, indicating favourable adsorption.

Table 5. A comparative evaluation of the adsorbent capacities of various types of adsorbents for the adsorption of some yellow dyes

Name of the dye	**Adsorbent**	**q_{max} (mg/g)**	**References**
Astrazon Yellow	Sepiolite	62.5-	Tekbaş et al., 2009
Astrazon Yellow	Wheat bran	82.5	Sulak et al., 2007
Astrazon Yellow	Apricot stone	69.09	Demirbas et al, 2008
Basic Yellow	Amberlite	221.23	Yener et al, 2006
Basic Yellow	Clinoptilolite	8.7	Yener et al, 2006
Reactive yellow 176	Biomass fly ash	59.6	Pengthamkeerati, et al.,
Supronal yellow 4GL	Montmorillnite	3.65	2008
Sunset yellow	Powdered peanut	58.47	Bouberka et al. 2006
Astrazon Yellow	hull	13.99	Gong et al., 2005
	Sawdust	81.77	In this study

3.7 Single stage batch adsorption

The schematic diagram for a single-stage adsorption process is shown in Figure. 9. The solution to be treated contains V l solvent, and the dye concentration is reduced from C_0 to C_e (mg L^{-1}) in the adsorption process. The adsorbent is added to the extent of m g adsorbate-free sawdust, and the solute dye concentration increases from q_0 to qe (mg g^{-1}). If fresh adsorbent is used, q_0=0. The mass balance equates the dye removed from the liquid to that picked up by the solid (Doˇgan el al., 2008)

$$V\left(C_0 - C_e\right) = m\left(q_e - q_0\right) = mq_t \tag{16}$$

The Langmuir data may now be applied to Equation 16 and substituting for q_e from Equation 14 and rearranging gives

$$\frac{m}{V} = \frac{C_0 - C_e}{q_e} = \frac{C_0 - C_e}{\left(\dfrac{q_{\max} b C_e}{1 + b q_{\max}}\right)} \tag{17}$$

Equation 17 permits analytical calculation of the adsorbent solution ratio for a given change in solution concentration, C_0 to C_e. A series of plots are shown in Figure 10. Figure 10 shows a series of plots derived from Equation 17 for the adsorption of A.Y on sawdust. An initial dye concentration of 100 mg. L^{-1} at 293Kand pH 7.5 is assumed, and the figures show the amount of effluent which can be treated to reduce the dye content by 10,20,40, 60,80 and 100% using various masses of adsorbent.

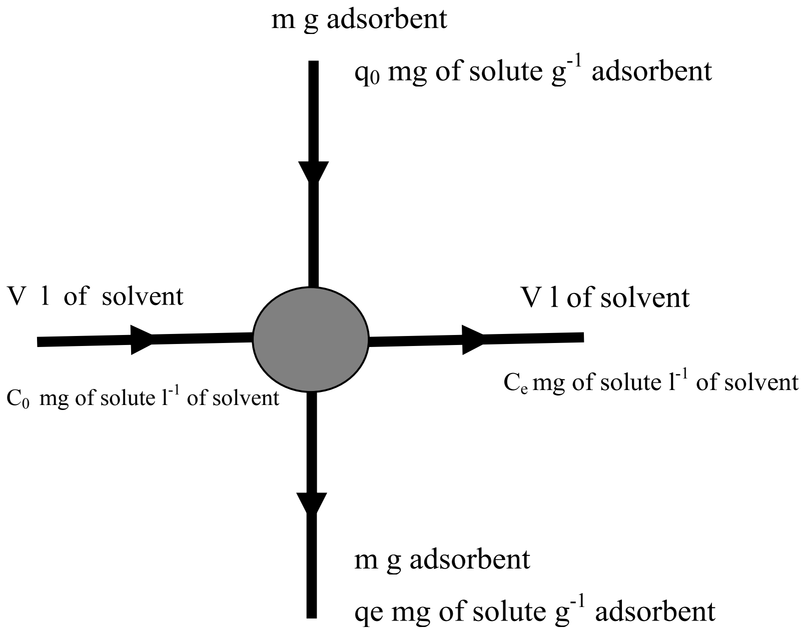


Figure 9. A single-stage batch adsorber

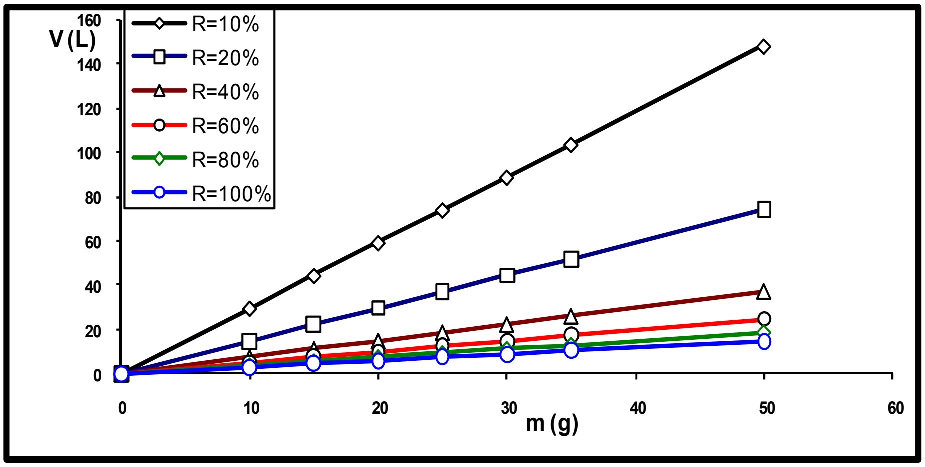
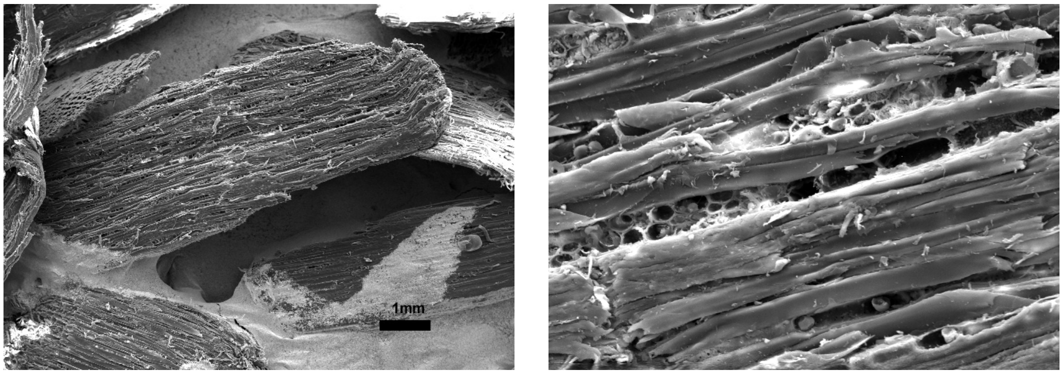


Figure 10. Volume of effluent (V) treated against adsorbent mass (m) for different percentages of A.Y removal

3.8 Instrumental analysis of adsorbent

3.8.1 SEM imaging

The adsorbent used in this study was analysed by Scanning Electron Microscopy to examine its textural structure. SEM analysis was carried out using JEOL 840 LGS. The SEM image (see figure 11) shows the porosity and surface structure. The adsorbent appears to have a rough surface and pores containing a new shiny and bulky spots. Since adsorption is a surface phenomenon, the rate and extent of adsorption are functions of the specific porous surface of the adsorbent used. The morphology shows a qualitative porosity varying from 20 to 50 µm. It appears also that the surface was constituted of different sizes and shapes, which indicates that the adsorbent has a porous structure (Lima et al., 2008). This surface property should be considered as a factor for providing an increase in the total surface thereby increasing the uptake capacity (Bayramo˘glu et al., 2006)



Enlarging x 34 Enlarging x 284

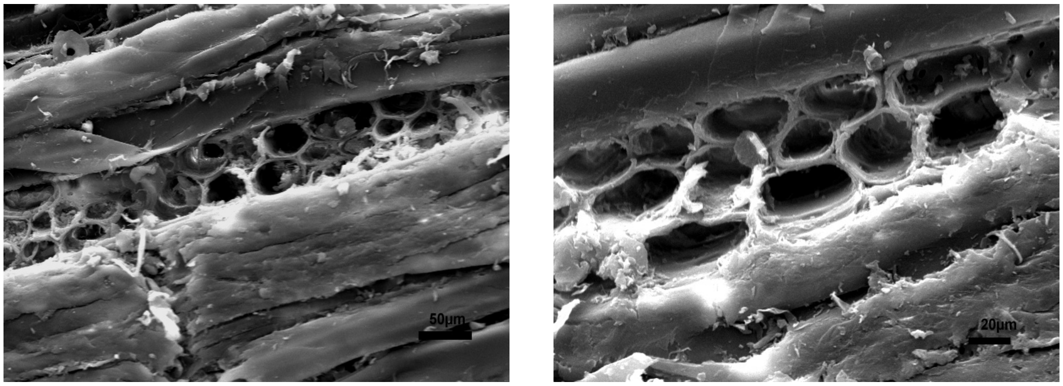


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Figure 11 SEM micrographs of the adsorbent (sawdust) before the adsorption

3.8.2 Fourier Transform Infrared Analysis (FTIR)

FTIR analysis of the sawdust (Aleppo Pine-tree) biomass was done to predict the functional groups responsible for the Astrazon Yellow adsorption. This was done by mixing approximately 5.0 mg dried sample of sawdust with 300 mg KBr (5:300), ground to fine powder and pressed under vacuum to a pellet. The pellet was analysed in the range 4000–400 cm−1. FTIR spectra were obtained using a Perkin Elmer "spectromum one" spectrometer

The profile by FTIR spectroscopy for sawdust is shown in Figure 12. The functional groups suggested here agree with those reported in other sawdust studies (Ahmad et al., 2009; Wan Ngah et al., 2008; Memon et al., 2007; Shukla et al., 2002).

FTIR spectra (see figure 12) showed the presence of characteristic absorption bands of Hydroxyl groups (–OH), Aromatic ring (C=C), Olefin (-C=C-), Aldehyde/Ester (-C=O), Lignin and Cellulose (C-O-H), cyclic ether group of cellulose (C-O). A complete list of absorption peaks and band assignment is given in Table 6. The cell walls of sawdust mainly consist of cellulose and lignin and many hydroxyl groups, such as tannins or other phenolic compounds. Lignin is a polymer material built up from the phenyl propane nucleus, an aromatic ring with a three-carbon side chain. Tannins are complex polyhydric phenols, which are soluble in water. Sawdust (of Aleppo Pine-tree) contain a number of phenolic OH^- group as well as C-O-H $^-$ group and -C=O which are believed to be the active sites for attachment of cationic dye.

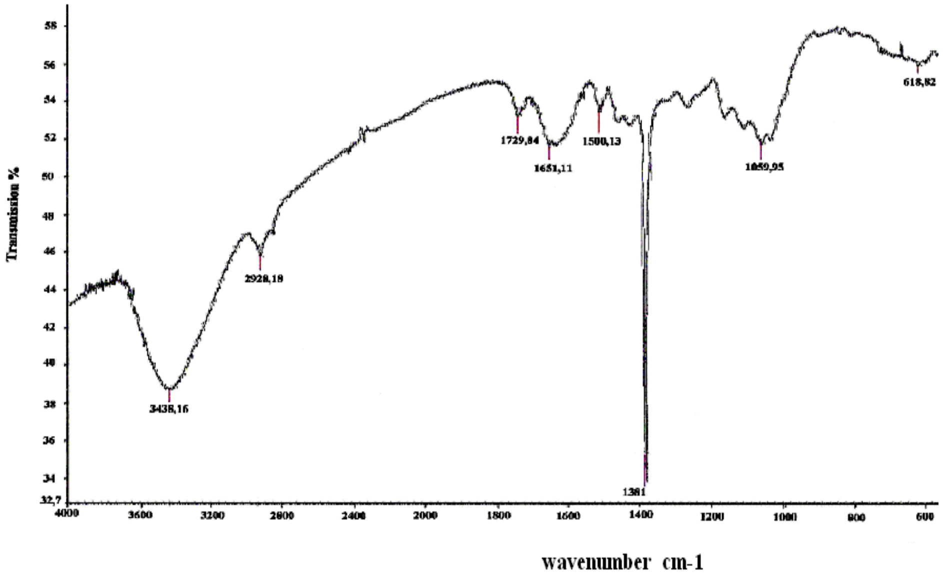

Figure 12. FTIR spectra of Sawdust biomass

Hence at higher pH, the surface of sawdust particles may become negatively charged, which enhances the positively charged Astrazon Yellow cations through electrostatic forces of attraction as seen earlier.

Table 6. IR absorption bands and corresponding possible groups

Functional group	Frequency (cm^{-1})
-OH	3438.16
C-H	2928.18
-C=O	2928.18
-C=C-	1651.11
C=C	1500.13
C-O-H	1381
C-O	1059.95

4. CONCLUSION

The results of present investigation show that sawdust (of Aleppo Pine-tree) has considerable potential for the removal of Astrazon Yellow from aqueous solution over a wide range of concentration. The adsorbed amounts of Astrazon Yellow increased with decreasing particle size of sawdust due to the increasing in the surface area. An increase in the initial dye concentration enhances the interaction between A.Y and sawdust, resulting in greater adsorption capacity. The dyes adsorption capacity increased with the increase of pH in the range of 2–9. The results showed that the adsorption system could be explained by the electrostatic attraction between the negatively charged surface and the positively charged dye molecule in the basic medium

The adsorbed amounts of A.Y increased with increase in contact time and reached the equilibrium after 300 min. The equilibrium time is independent of initial AY concentration. The equilibrium data have been analyzed using Freundlich and four types of the Langmuir (Type 1-4) isotherms. It was observed that the sorption data fitted better (RMSE = 2.18) to the Langmuir model (type 1) than Freundlich and others types of Langmuir isotherm models. The kinetics of adsorption of AY on sawdust was studied by using fractional Power model, pseudo first- and second-order equations, intraparticle diffusion equation and the Elovich equation. The Elovich equation provided the best correlation of the experimental data, which describes chemical adsorption mechanism (chemisorption) being the rate controlling step. The adsorption of AY on sawdust can also be successfully interpreted by the pseudo second-order equation based on the adsorption capacity on the solid phase and is in agreement with a chemisorption mechanism. Overall, sawdust (of Aleppo Pine-tree) shows excellent adsorptive characteristics for the removal of Astrazon Yellow due its high uptake capacity and to its low cost.

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