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Removal of acid yellow-17 dye from aqueous solution using eco-friendly biosorbent

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ABSTRACT

Dyes are usually present in trace quantities in the treated effluents of many industries. The effectiveness of adsorption for dye removal from wastewaters has made it an ideal alternative to other expensive treatment methods. Biosorption of acid yellow (AY17), a monoazo acid dye, was investigated using *Typha angustata* L. as biosorbent in a batch system with respect to initial pH, temperature, initial dye concentration, biosorbent dosage, and contact time. The biomass exhibited the highest dye uptake capacity at 303 K, initial pH value of 2, the initial dye concentration of 150 mg/L, biosorbent dosage of 0.5 g and contact time of 40 min. The extent of dye removal increased with increase in time, biosorbent dosage and decreased with increase in temperature. The equilibrium sorption capacity of the biomass increased on increasing the initial dye concentration up to 150 mg/L and then started decreasing in the studied concentration up to 600 mg/L. The experimental results have shown that the acidic pH favors the biosorption. Langmuir and Freundlich adsorption model is used for the mathematical description of the biosorption equilibrium and isotherm constants are evaluated at different temperatures. Equilibrium data fitted very well to the Freundlich model in the studied concentration (25–600 mg/L) and temperature (303–323 K) ranges. The pseudo-first- and second-order kinetic models were also applied to the experimental data. The results indicated that the dye uptake process followed the pseudo-second-order rate expression and the adsorption rate constants increased with increasing concentration. The adsorption results in this study indicated that all the adsorbents were attractive candidates for removing acidic dyes from dye wastewater.

Keywords: Wastewater treatment; Acid yellow dyes; Color removal; Adsorbents; Isotherm; Kinetics; *Typha angustata* L.

1. Introduction

Dyes are the most easily recognizable pollutants in the environment because of their appearance. Dyes are a large and important group of industrial chemicals for which world production in 1978 was estimated at 640,000 tons [1,2]. Various kinds of synthetic dyestuffs appear in the effluents of wastewater in various industries such as textiles, leather,

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paper, carpet, printing, etc. but textile industry is totally based on dyes to color the fabric. As far back as in 3500 BC, the natural dyes extracted from vegetables, fruits, flowers, certain insects, and fish were being used to dye fabric [3,4]. With the discovery of synthetic dyes by WH Perkins in 1856, the use of synthetic dyes gave way to natural dyes that gave a limited and dull range of colors that had lower fastness to light and washing [5]. More than 3,600 individual textile dyes are being manufactured by the industry today [6]. The daily water consumption of an average sized textile mill having a production of about 8,000 kg of fabric per day is about 1.6 million liters [7]. Dyeing section contributes to 15–20% of the total waste water flow [8,9].

Due to their good solubility, synthetic dyes are common water pollutants and they may frequently be found in trace quantities in industrial wastewater. However, the discharge of dye-bearing wastewater into natural streams and rivers possess a severe environmental problem. The entire wastewater may contain elements like sulfur, naphthol, vat dyes, nitrates, acetic acid, soaps, and chromium compounds and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt and certain auxiliary chemicals all of which collectively make the effluent highly toxic [10] Other harmful chemicals present in the water may be formaldehyde-based dye-fixing agents, chlorinated stain removers, hydro carbon-based softeners, and nonbiodegradable dyeing chemicals [11]. All these organic materials are of great concern in water treatment because they react with many disinfectants to form by-products (DBP'S) that are often carcinogenic and, therefore, undesirable. Many of these show allergic reactions particularly benzidine or arylamine-based dyes are well known for their carcinogenity [12]. Disperse dyes have been shown to have high partition coefficients and solubility, suggesting significant potential for bioconcentration [13]. The colloidal matter present along with colors and oily scum increases the turbidity, gives the water a bad appearance, and prevents photosynthesis [14]. Dyes in the wastewater undergo chemical as well as biological changes, consume dissolved oxygen from the stream, and destroy aquatic life because of their toxicity (as dyes impart toxicity to aquatic life and are damaging the esthetic nature of the environment). In addition, when this effluent is allowed to flow in the fields it clogs the pores of the soil resulting in loss of soil productivity [15]. If allowed to flow in drains and rivers it effects the quality of drinking water in hand pumps making it unfit for human consumption [16]. Such polluted water can also be a breeding ground for bacteria and viruses. A lot of well established literature is already available on the role of dyes as a major cause in skin and respiratory diseases in human beings [17–20].

Similarly, these industries generally have difficulty in meeting wastewater discharge limits, particularly with regard to dissolved solids, ionic salts, pH, chemical oxygen demand, color, and sometimes heavy metals [21]. The problem of color in wastewater effluent and the possible problems associated with the discharge of dyes and dye degradation products are of concern. It is therefore necessary to treat these effluents prior to their discharge into the receiving water. However, wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light, heat, and oxidizing agents due to their structure and molecular size [22,23].

Traditional methods for the treatment of aqueous streams to eliminate dyes are usually the biological, physical, and chemical techniques as well as the various combinations; chemical coagulation followed by sedimentation [24] and adsorption are the widely used ones [25], but other advanced techniques are often applied, e.g. UV [26,27], ozonation [28], ultrasonic decomposition, or combined oxidation processes [29–31]. Amongst the numerous techniques of dye removal, adsorption is the procedure of choice and gives the best results as it can be used to remove different types of coloring materials [32]. If the adsorption system is designed correctly it will produce a high-quality treated effluent. Adsorption techniques have gained favor in recent years because of their proven efficiency in the removal of pollutants from effluents too stable for conventional treatment methods [33–35]. Activated carbon (powdered or granular) is the most widely used adsorbent because it has excellent adsorption efficiency for organic compounds, but its use is usually limited due to its high cost [36]. In order to decrease the cost of treatment, attempts have been made to find inexpensive alternative adsorbents. Consequently, a number of low cost and easily available materials, such as waste biomass, are being studied for the removal of different dyes from aqueous solutions at different operating conditions [37]. Treatment by biosorption has been investigated in recent years enormously using different waste materials of agricultural or industrial origin like coir pith, bottom ash, egg shells, fishery waste, leaves of neem, globe artichoke and pine, radish peels, peas waste, orange peels, cassava peel, saw dust, rice husk, eucalyptus bark, wheat husk, etc. [38–46]. The main purpose of searching new biosorbents is to replace activated charcoal and ion exchange resins, which are very expensive to use on larger scale but

Table 1
Adsorption capacities of some biosorbents against different dyes

Sr no.	Biosorbent	Dye	$q_{\max}$ (mg/g)	Reference
1	Saw dust-cherry	Acid blue25	31.98	[52]
2	AC-pinewood	Acid blue 264	1,176	[53]
3	Wood	Basic blue 69	100.1	[54]
4	Peat	Basic blue 69	0.43–0.91	[55]
5	Rice husk	Basic blue 9	312	[56]
6	Beer brewery waste	Basic blue 9	4.92	[57]
7	Spent tealeaves	Methylene blue	300.052	[58]
8	Orange peels	Direct red 23	10.72	[59]
9	Sunflower stalk	Congo red	37.78	[59]
10	Plam oil ash	Disperse blue	49.5	[60]

more efficient. The researchers are trying to find an alternative biosorbents of biodegradable origin and cheap nature with great biosorptive efficiencies and are searching new ways to modify biosorption capacities, either by physical or chemical modification [47,48]. Table 1 shows the comparison for adsorption of some dyes on various adsorbents.

The present work deals with a series of experiments to assess the utility of *Typha angustata* L. as a biosorbent for the removal of acid yellow dye from aqueous solution. Acid yellow-17 dye is a reactive, anionic, textile dye having general formula shown in Fig. 1. It is usually employed in detergent, soap, textile, printing, and cosmetic industries. It is also marketed with the other names like fluorescein or its sodium salt and uranin. It can harm respiratory system, i.e. dyspnea, dermatitis, and irritation to eyes, and cardiovascular and nervous system of human beings and living organisms. Its thermal decomposition produces toxic fumes of oxides of carbon and nitrogen. It has mutagenic and tumorigenic effects on bacteria, yeast, and somatic cells of mammalian, resulting in problem during reproduction and growth by affecting genetic material [49,50]. Therefore, its removal from wastewater is a critical issue.

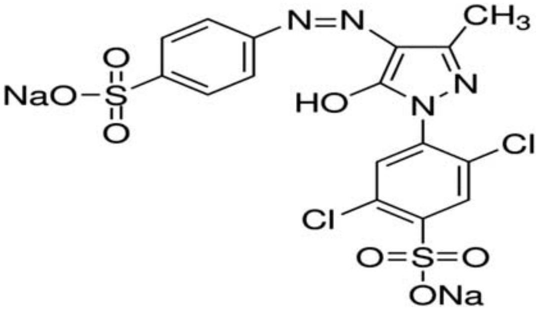


Fig. 1. Molecular structure of acid yellow-17 dye.

T. Angustata L. is used as a novel biosorbent for treating acid yellow-17 dye. *T. Angustata* L. is low cost, biodegradable, and poses no disposal problems. It is the plant which grows in the marshy places with a lot of abundance. It is the very common plant in arid regions of Asian countries like Pakistan, India, Bangladesh, and Sri Lanka. It belongs to the plantae kingdom. Typhaceae is the family name and the name of its species is *T. Angustata* L. It had been studied as a potential biosorbent for the removal of heavy metals [51,52].

The aim of the present study is to investigate the adsorption behavior of acid yellow-17 on low cost *T. Angustata* L. adsorbent under different experimental conditions. Therefore, the optimum conditions of contact time, pH, initial dye concentration, biosorbent dose, and temperature were determined using acid yellow as an initial dye model, some known kinetic equations have also been evaluated. The Langmuir equation was used to fit the equilibrium isotherm. The effects of solution pH on adsorption capacity were also studied. The dynamical behaviors of the adsorption were measured on the effect of initial dye concentration. The adsorption rates were determined quantitatively and stimulated by the nonlinear first-order and second-order models.

2. Materials and methods

2.1. Preparation and characterization of biosorbent

Raw biosorbent *T. Angustata* L. was obtained from the marshy bank of seasonal canal situated in the out skirt of Jhang City, District Jhang, Punjab Province, Pakistan. Biosorbent was dipped in tap water for 6 h and then washed to remove the mud. Afterwards, it was air-dried. Then it was ground into fine powder. At this point, biosorbent was washed with distilled water. Then soaked in distilled water and kept overnight to remove any biological impurities like chlorophyll, etc. which could interfere in light-absorbing phenomenon later on. Overnight soaking was repeated one more time. The material was washed repeatedly till all the coloring bodies were removed. Then material was oven-dried at controlled temperature (100℃) to evaporate any kind of moisture from the bulk. The oven-dried material (200 g) was then modified with 0.25 N NaOH solution in order to completely neutralize the biosorbent. The modification of *T. Angustata* L. biosorbent with NaOH was carried out as follows: for each gram of biomass 20 ml of 0.1 mol L^{-1} NaOH solution was added; then the mixture was agitated; and during 2 h the supernatant was discharged. Next, the material was repeatedly washed with deionized water and dried at 60˚C for 24 h to study the adsorption of dye by modified biosorbent (MTA) in comparison with unmodified biosorbent (TA). MTA was dried at 60˚C as compared to TA at 100˚C as the increased temperature can disturb the binding sites after modification. The two biosorbents were then sieved to obtain particle sizes of 200, 400, and 800 μm and finally, stored in air tight containers to be used subsequently.

2.2. Point of zero charge

Point of zero charge (PZC) is the pH at which the biomass surface has a neutral charge. In this study, the methodology chosen for study PZC was described by Guilarduci et al. [48]. This procedure consisting of mixing 0.5 gm of the biomass with 50 ml of an aqueous solution at different initial pH values (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12) adjusted at 30˚C using NaOH and HCl solutions. The ionic strength of the solution was varied by adding 0.01, 0.1, and 0.5 mol L^{-1} of KCl, which results in three PZC values for each biomass sample. After reaching equilibrium (24 h), the final pH was measured making it possible to construct a final pH vs. initial pH plot based on these data and the PZC pH referred to the final pH constant value was determined. All the analysis was carried out in duplicate.

2.3. SEM analysis

The surface morphology of the modified and unmodified biomass samples was investigated using a Scanning electron microscopy (SEM) JEOL JSM-6460LV. Biomass samples were firstly attached to 10 mm alumina-based mounts using double-sided tape, sputter-coated with gold using a 30 mA current for 180 s, at working distance of 50 mm (BAL-TEC-SCD005, Balzers, Germany), under vacuum in an argon atmosphere, in order to achieve their surface conductivity. An accelerating voltage of 25 kV for primary electrons as well as working distance of 10 mm was proved to be satisfactory. Spot sizes varied from 25 to 40 nm depending on the applied magnification. Speed 3, offered by software as "fine" scan, was chosen because of the occasional problems with Speed 4, known as "super fine" scan rate, manifested as "floating" of images at higher magnifications.

2.4. FTIR spectrum of biomass

Biosorbents were then used for FTIR analysis based on the biosorption capacities for acid yellow-17. Fourier transform infrared spectroscopy (FTIR) spectra of MTA and TAs were recorded using a Nicolet 5700 spectrophotometer (Thermo, USA) in the 400–4,000 cm wavelength region. FTIR characterization was performed in order to identify chemical functional groups present on the biomass that might be involved in the metal uptake procedure. The obtained FTIR spectra were analyzed using Win Bomem Easy software.

2.5. Preparation of dye solution

Acid yellow-17 (C.I. = 18,965, Chemical formula = $C_{16}H_{10}Cl_2N_4Na_2O_7S_2$ FW = 551.29, and nature = acid yellow-17) was obtained from Shafi Razo Co. Ltd. Stock solution (1,000 ppm or mg/L) of dye was prepared by dissolving 1 g of the dye in dist. Water and volume was increased up to 1 liter by adding dist. water afterwards. Its pH was determined to be 6 by pH meter. Then, stock solution was diluted up to different concentrations (e.g. 5 ppm, 10 ppm, 15 ppm, or 20 ppm) for subsequent experimental work. For this purpose dilution formula was used.

$$C_1V_I = C_2V_2$$

2.6. Analytical measurements

The concentration of the dye was determined using a UV–vis spectrophotometer (HITACHI U 2000 spectrophotometer) at a wavelength corresponding to the maximum absorbance of the dye (max = 401.5 nm). Calibration curves were plotted between absorbance and concentration of the dye solution. The absorbance was recorded for different concentrations of solutions of dye by using visible spectrophotometer. Arbitrarily, 10 ppm concentration was selected because it gave absorbance lesser than one. Now absorbance was recorded by varying wavelength in visible region, i.e. 380–780 nm. At first, absorbance was recorded after a difference of 20 nm. Ultimately, the wavelength at which 10 ppm concentrated solution absorbed maximum light was sorted to be 485 nm.

2.6.1. Drawing the calibration curve

Calibration curve is the graph drawn for the absorbance of light by the acid yellow-17 dye as a function of concentration. This graph helps in determining the concentration of dye remaining in the solution or the amount of dye adsorbed on biosorbent at any time, with the help of linear equation.

$$Y = mX + C$$

where Y represents the absorbance, X represents the concentration of dye (mg/L), m is the slope of linear equation, and C is the intercept of the graph line.

2.6.2. Determination of equilibrium time (t_e)

Equilibrium time is the time which is taken by the biosorbent to adsorb maximum amount of dye, denoted by t_e.

Two measuring flasks of 100 cm^3 volume were taken. The 50 cm^3 of 10 ppm concentration dye solution was placed in each flask and was put on the orbital shaker. The 0.2 g of TA was added to one of the two flasks. This was the sample flask and the other served as the blank flask. These were shaken at constant speed. Samples were taken out from both flasks at regular intervals of time, centrifuged and absorbance of the supernatant was recorded for each sample. The concentration of dye in solution decreased at high rate at the start of the experiment and then got steady. The time at which concentration became constant was taken as equilibrium time t_e.

2.6.3. Calculation of uptake capacity (q_e)

The uptake capacity by the biomass was calculated by the following formula:

$$q_e = (C_0 - C_e)\ \mathrm{V/w}$$

where q_e is the uptake capacity in mg of adsorbate per gram of the adsorbent, V is the volume of the solution in liters, and w is the mass of adsorbent in grams.

2.6.4. Effect of change in initial concentration of solution on adsorption

In this experiment, the effect of change in initial concentration of solution on adsorption of dye was studied by keeping the other variables (pH of solution, temperature of solution, particle size of biosorbent, and biosorbent dose) constant. Change in absorbance, as a function of time, was recorded for various concentrations (5, 10, 15, and 20 ppm) up to equilibrium time. Dye concentration was measured using the same procedure adopted for equilibrium time.

2.6.5. Effect of change in pH of solution on adsorption

Effect of change in pH of dye solution was studied by keeping the other variables (concentration of solution, temperature of solution, particle size of biosorbent, and biosorbent dose) constant. Change in absorbance, as a function of time, was recorded for pH values 2, 4, 8, and 10 up to equilibrium time (70 min). For this experiment, each time pH of solution was maintained by using buffer tablets. Dye concentration was measured using the calibration curve. Buffer tablets were used to maintain the pH of the solution.

2.6.6. Effect of change in particle size on adsorption

Change in particle size of biosorbent affects the adsorption phenomenon. It was studied by keeping the other variables (pH of solution, temperature of solution, and concentration of solution and biosorbent dose) constant. Change in absorbance, as a function of time, was recorded for particle sizes 200, 400, and 800 μm up to equilibrium time (70 min). Concentration of dye present in the solution at any time was calculated with the help of calibration curve.

2.6.7. Effect of change in temperature on adsorption

In this experiment, the effect of change in temperature of solution on adsorption of dye was studied by keeping the other variables (pH of solution, concentration of solution, particle size of biosorbent, and biosorbent dose) constant. Change in absorbance, as a function of time, was recorded at 303, 313, 323, and 333 K up to equilibrium time (70 min). To maintain the temperature during experiment, hot plate was used. Dye concentration was calculated with the help of calibration curve.

2.6.8. Effect of change in biosorbent dose on adsorption

In this experiment, the effect of change in biosorbent dose on adsorption of dye was studied by keeping the other variables (pH of solution, temperature of solution, concentration of solution, and particle size of biosorbent) constant. Change in absorbance, as a function of time, was recorded by adding 0.1, 0.2, 0.3, and 0.5 g per 50 mL of solution in the sample flask. Biosorbent was shaken for the sorted equilibrium time (70 min). Calibration curve was used to determine the dye concentration present in the solution at any time from the corresponding value of absorbance.

2.7. Adsorption isotherms

Adsorption isotherm is actually an equilibrium–time relationship between amount of adsorbate per unit mass of adsorbent (q_e in mg/g) and concentration of adsorbate solution at equilibrium time (C_e in mg/L) [19]. It is useful for calculating the maximum amount of adsorbate taken up by adsorbent (uptake capacity) [19]. There are several isotherms which help for the said calculations; however, Freundlich isotherm and Langmuir isotherm are commonly in practice.

2.7.1. Freundlich isotherm

It is an empirical equation which describes the adsorption process as heterogeneous phenomenon. Its characteristic feature is the heterogeneity factor $1/n$. Equation of Freundlich isotherm is given as follows [53].

$$q_e = K_F C_e^{1/n} \tag{1}$$

Here, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent measured in (mg/g), K_F is the Freundlich constant measured in $(\mathrm{mg/g}) \cdot (\mathrm{L/mg})^{1/n}$, C_e is the concentration of adsorbate in liquid at equilibrium time measured in (mg/L), and $1/n$ is the heterogeneity factor.

Linear form of the Freundlich equation is:

$$\log q_e = \log K_F + 1/n \cdot \log C_e \tag{2}$$

Graph is plotted between log q_e and log C_e values and a straight line is obtained having slope equal to $1/n$ and intercept equal to log K_F. If the value is greater than 1 then adsorption is considered favorable [54].

2.7.2. Langmuir isotherm

It is the most popular isotherm for the analysis of adsorbing data. It best describes the mono layer adsorption mechanism. Langmuir's equation is given as follows [55].

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C} \tag{3}$$

Here, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent measured in (mg/g), C_e is the concentration of adsorbate in solution at equilibrium time measured in (mg/L), $q_{\max}$ is the maximum adsorption capacity of adsorbent corresponding to the monolayer coverage of surface measured in (mg/g), and K_L is the Langmuir constant measured in (L/mg).

Linear form of the Langmuir equation is:

$$C_e/q_e = 1/q_{\max} \cdot K_L + C_e/q_{\max} \tag{4}$$

Graph is plotted between C_e/q_e and C_e. Straight line is obtained having intercept equal to $1/q_{\max}$. From the value of K_L, another parameter, R_L, is calculated. It is a dimensionless separation factor and can be calculated by the following equation:

$$R_{\mathrm{L}} = \frac{1}{1 + K_{\mathrm{L}} C_0}$$

If the value of R_L is greater than 1 then adsorption is unfavorable, if it is equal 0 then adsorption is linear, if it is between 0 and 1 then adsorption is considered favorable, while the value of R_L smaller than 1 represents irreversible mode of adsorption.

2.7.3. Temkin's isotherm

It is basically the study of the effect made on the heat associated with adsorption process because of the relationship between different adsorbate and adsorbent. It suggests that because of this indirect interaction, the heat associated with adsorption process decreases linearly. Equation of the isotherm is as follows [56].

$$q_e = RT/b \cdot \ln(A C_e) \tag{5}$$

Linear form of the above equation is:

$$q_e = RT/b \cdot \ln A + RT/b \cdot \ln C_e \tag{6}$$

If $RT/b = B$ then above equation becomes,

$$q_e = B \ln A_t + B \ln C_e \tag{7}$$

where q_e is the amount of adsorption measured in (mg/g) corresponding to equilibrium time, C_e is the concentration of adsorbate in solution at equilibrium time measured in (mg/L), B is the constant related to heat, and A_t is also the constant for Temkin's equation. Values of constants A_t and B can be determined by the graph plotted between q_e and ln C_e.

2.8. Kinetics of the adsorption

Rate of adsorption of dye on adsorbent is the subject of kinetic study of adsorption. Kinetics of the adsorption is studied by different models. In the present study, pseudo-first-order model, pseudo-second-order model, and intra-particle diffusion model are used for the purpose.

2.8.1. Pseudo-first-order kinetics model

Lagergren proposed pseudo-first-order equation to be used for elucidating the rate of adsorption. Equation is given as follows [57]:

$$dq_t/d_t = k_1(q_e - q_t) \tag{8}$$

Here, k_1 represents rate constant of pseudo-first-order measured in (min^{-1}), q_t is the amount of adsorption at any time measured in (mg/g), while q_e represents the amount of maximum adsorption (corresponding to the equilibrium time) also measured in (mg/g).

After integrating between the limits $t = 0$ to t for time and $q_t = 0$ to q_t for the amount of adsorption, the above equation becomes,

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{9}$$

A graph plotted for the values of t along X-axis vs. log ($q_e - q_t$) along Y-axis gives the straight line. Values of q_e and k_1 can be calculated from the slope and intercept of the above equation.

2.8.2. Pseudo-second-order kinetics model

Pseudo-second-order kinetics model is represented with the following equation [58]:

$$dq_t/d_t = k_2(q_e^2 - q_t)^2 \tag{10}$$

Here, k_2 is the rate constant for pseudo-second-order model measured in (g/mg min), q_t is the amount of adsorption at any time measured in (mg/g), while q_e represents the amount of maximum adsorption (corresponding to the equilibrium time) measured in (mg/g).

Applying the limits $t = 0$ to t for time and $q_t = 0$ to q_t for the amount of adsorption and integrating the above equation becomes,

$$t/q_t = 1/K_2 q_e^2 + (1/q_e)t \tag{11}$$

This is the equation of straight line. The values of second-order rate constant K_2 and adsorbing capacity at equilibrium time (q_e) can be determined from the slope and intercept of above equation.

2.8.3. Intra-particle diffusion model

Sometimes adsorption may follow the intra-particle diffusion mechanism, i.e. adsorption may not be limited to external surface of the adsorbent only. This step of intra-particle diffusion may be the slowest (rate determining) step. For studying the kinetics of such systems intra-particle diffusion model was proposed by Webber and Morriss. Equation of the intra-particle diffusion model is given as follows [59]:

$$q_t = k_{\text{dif}}\sqrt{t} + c \tag{12}$$

Here, k_{dif} is the intra-particle diffusion rate constant measured in $\text{mg/g min}^{1/2}$.

While q_t is the amount of adsorption at any time measured in mg/g. A graph plotted between q_t values and square root of time values gives the straight line. Values for K_{dif} can be calculated from the slope of graph line drawn between values q_t (up-taken amount of adsorbate) and $\sqrt{t}$ (square values of time). Equation of intra-particle diffusion model suggests that q_t should be the linear function corresponding to $\sqrt{t}$ values [60]. Line should pass through the origin if intra-particle diffusion mechanism is the mode adsorption. The value of intercept decides about this issue, if intercept has greater value then the line does not pass through the origin, this neglects the intra-particles diffusion. Conversely, if intercept has smaller value then the intra-particle diffusion mode may be the mode adsorption presumably.

3. Results and discussion

A series of experiments was carried out to investigate the effect of different operating conditions on the rate of electrochemical degradation of the investigated dyes.

3.1. Morphological characteristics of the biomass

The SEM image in Fig. 2(A) shows a highly porous morphology of the raw biomaterial with pores of more or less different shapes and sizes. This figure also reveals the existence of plant vessels of horizontal as well as vertical orientations and a variety of cavities on the external surface. These may

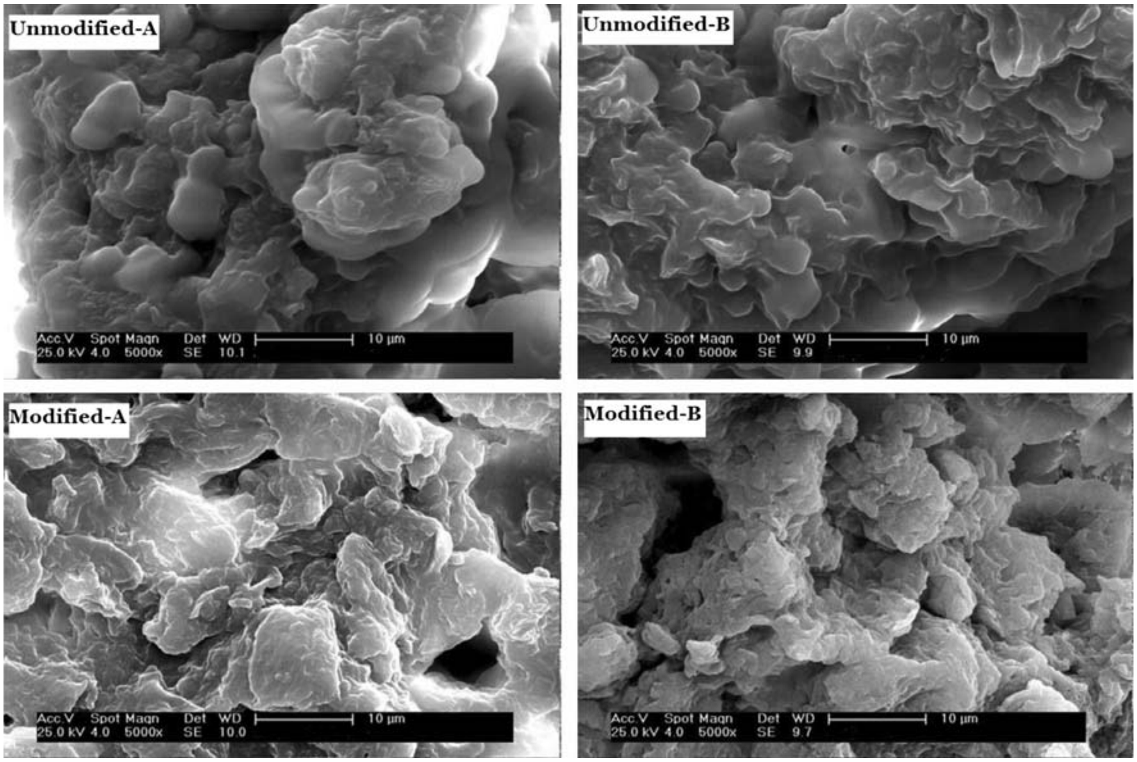


Fig. 2. Scanning electron microscope (SEM) image of MTA and TAs.

contribute to the relatively high surface area of the biomaterial. Such biomaterial refined with sodium hydroxide, and further playing the role of biomass in the adsorption process. Fig. 2(B), exhibits somewhat changed morphology with extended surface arrangement regarding the repetition of structures, plant vessel orientations, the subsistence of pores of comparable shapes and sizes, and the smallest openings becoming more available for reactants. One of the reasons for this change may be the removal of the alkaline and alkaline earth metals during refinement, which could contribute to the changes in morphology.

Table 2
The FTIR spectral characteristics of TA and MTAs

Wavelength range (cm^{-1})	Biosorbent		Differences	Assignment
	TA	MTA		
3,100–3,500	3409.3	3439.8	+30.5	N–H stretching
2,700–2,950	2925.2	2925.8	+0.6	–CH stretching
2,700–2,950	2854.4	2855.1	+0.7	–CH stretching
1,750–1,680	1745.1	1744.5	−0.6	C=O carbonyls
1,670–1,500	1635.0	1634.1	−0.9	Carboxylic groups
1,670–1,500	1543.7	1543.7	0	Carboxylic groups
1,490–1,350	1460.4	1460.1	−0.3	–CH bending vibrations
1,490–1,350	1379.1	–	–	–CH bending vibrations
1,300–1,000	1238.3	–	–	–SO_3 stretching
1,350–1,000	1155.7	–	–	O–H alcohols(primary and secondary) and aliphatic ethers
1,300–1,000	1078.6	1079.6	+1.0	C–O stretching of COOH

3.2. FTIR spectral analysis

The quality and quantity of sorption of dyes onto the biomass surface is strongly determined by functional groups present on the plant material [38,40]. Therefore, FTIR characterization was carried out to analyze the major functional groups which exist in the biosorbent (Table 2). Peaks appearing in the FTIR spectrum of *T. Angustata* L.-based biosorbent are assigned to various groups and bonds in accordance with their respective wavenumbers (cm^{-1}). The FTIR spectra for *T. Angustata* L. biosorbent confirmed changes in the availability of active functional groups and surface properties of the MTA (Table 2). From the difference of FTIR spectrum, it could be clearly delineated the major involvement of functional groups like $–NH_2$,–OH, $–SO_3$, –CH, and –COOH present on the biosorbent surface in the acid yellow-17 biosorption process (Table 2).

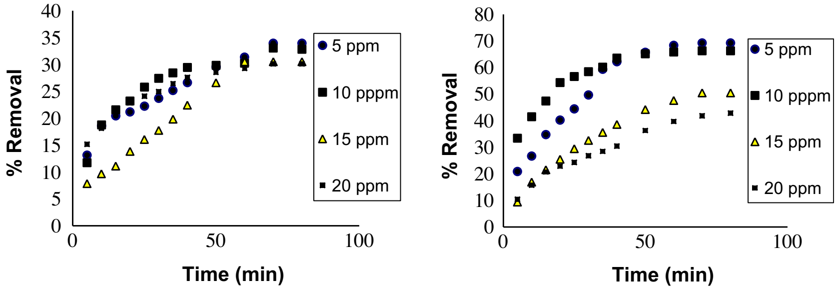
3.3. Determination of equilibrium time t_e for TA and MTA

Fig. 3 shows % removal of acid yellow-17 for different concentrations as a function of time and found that equilibrium time for TA was 70 min. Similar results were obtained with the MTA. This showed that the modification of biosorbent (TA) with NaOH did not change equilibrium time.

It is clear from graphs that % removal of dye increased rapidly at the beginning. As the time passed, % removal of dye did not increase as rapidly till it became constant at equilibrium time (t_e). It is because initially a large number of adsorption sites are present uncovered. With the passage of time, these sites are covered and when equilibrium is achieved no more adsorption takes place. That is why % removal of dye came to a constant level at equilibrium time.

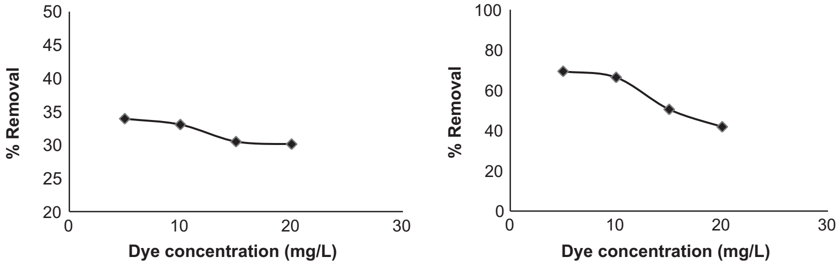
3.4. Effect of change in concentration on % removal of acid yellow-17

Biosorbent in unmodified and modified forms was shaken for the already sorted equilibrium time (70 min) with different initial concentrations of solution and % removal of dye was recorded. Fig. 4 represents % removal of dye as a function of initial concentration of solution for TA and MTAs, respectively.



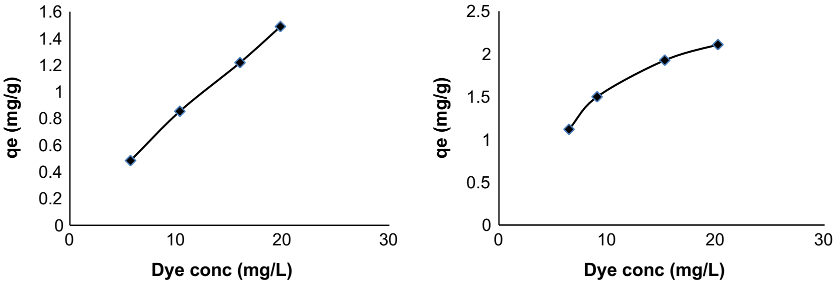
(a) TA (b) MTA

Fig. 3. Percent removal of acid yellow-17 by TA and MTA for different concentrations as a function of time.



(a) TA (b) MTA

Fig. 4. Percent removal of acid yellow-17 by TA and MTA as a function of concentration.



(a) TA (b) MTA

Fig. 5. Amount of acid yellow-17 dye adsorbed on TA and MTA as a function of concentration.

From the graphs, it is clear that % removal of dye decreased when the initial concentration was increased. It is because with higher initial concentration the sites available for sorption are covered in equilibrium time leaving behind the sufficiently enough concentration of dye in solution. As a result, % removal decreased for higher initial concentrations of solutions.

3.5. Effect of change in initial concentration on the amount of dye sorbed/uptake capacity q_e (mg/g)

Amount of dye sorbed per unit mass of TA and MTAs was calculated from the formula given in experimental section for different initial concentrations. Subsequently, it was represented in Fig. 5 for the two (TA and MTA) biosorbents, respectively. It is clear that q_e increased as the initial concentration of solution increased. Reason is that with increase in initial concentration more molecules of dye are available to be sorbed, so biosorbents take up more amount of dye, i. e. uptake capacity of biosorbents increases with higher initial concentrations of solution.

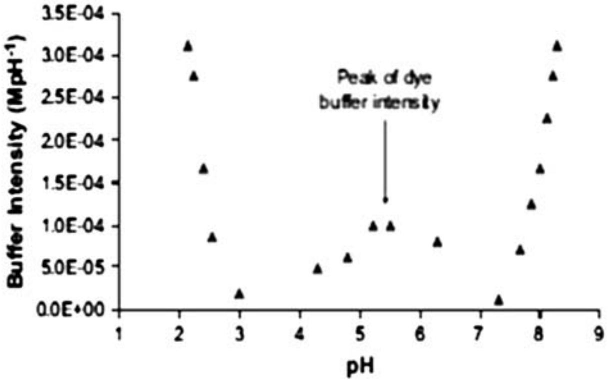


Fig. 6. Buffer intensity curve for C.I. acid yellow-17.

Table 3
Characteristic of acid yellow-17

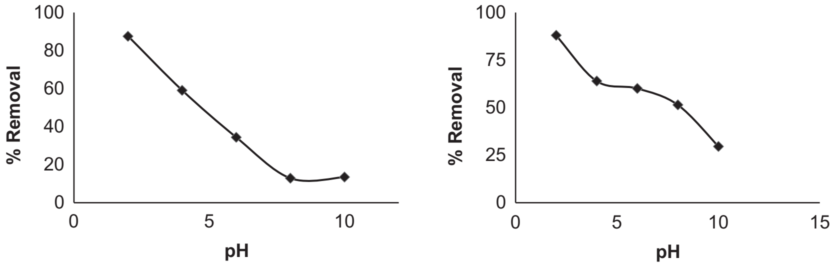
C.I. (generic name)		Acid yellow-17
$\lambda_{\max}$ (nm)		404
Solubility at 25℃ (gm/dm^3)		70.0
pK_a		5.3
C (wt.%)		34.5
Number of ionizable groups		3
Number of polar functional groups	–S–O	9
	–C–O	1
	–Cl	3
	–NH	2
	–NH2	–

3.6. Effect of change in pH on % removal of dye

The acidity constants (Ka) of the acid yellow-17 were 5.5. The acidity constants (Ka) for this particular dye have not been previously reported. The values of pK_a of the acid yellow-17 were determined using a standard potentiometric titration method [12]. Due to acid–base properties, dye can be titrated using suitable acid or base solution. The pK_a values of acid yellow-17 were calculated by plotting the equilibrium pH against buffer intensity of dyes (M pH^{-1}) [12]. Fig. 6 illustrates the variations in buffer intensity of C.I. acid yellow-17 against pH. The pK_a values were obtained from the maximum buffer intensity when the concen-

Table 4
pH buffer tablets

Description	Quantity	Part no.
pH buffer tablet 1	100 ct.	RT564-1BT
pH buffer tablet 1	100 ct.	RT563-1BT
pH buffer tablet 1	100 ct.	RT562-1BT
pH buffer tablet 1	100 ct.	RT561-1BT
pH buffer tablet 1	100 ct.	RT560-1BT



(a) TA (b) MTA

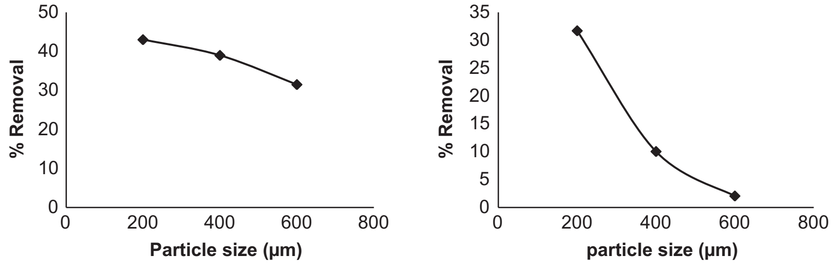
Fig. 7. Percent removal of acid yellow-17 by TA and MTA as a function of pH.

tration of ionized and neutral dye species was equal [12]. As shown in Fig. 6, the pK_a value of C.I. acid yellow-17 was 5.5. It was found that the reported pK_a values of acid yellow-17 were similar to those reported for other anionic dyes [32].

Table 3 summarizes the number of polar and ionizable functional groups that were present in dye molecules and contain much the same density of polar functional groups (15–18 groups/molecule) and ionizable groups (3–4 groups/molecule).

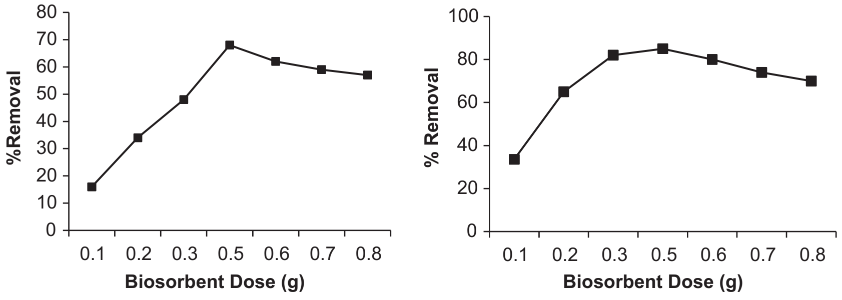
The effect of pH change on % removal of dye was studied from pH 3 to 10. The initial dye solution has a pH 3. The pH buffer tablets of Orbeco Hellige Co. were used for creating solutions of 1, 3, 5, 7, and 10 pH units by simply adding the tablet to 100 ml of deionized water and pH is measured by using pH meter 200 series by Orbeco Hellige Co. The name of the buffer tablets are given in Table 4.

Effect of pH on % removal of dye was studied by shaking TA and MTAs for equilibrium time (70 min) while keeping the other parameters, such as concentration, biosorbent dose, particle size, and temperature of the solution, constant. Fig. 7 represents that with an increase in pH % removal decreased. Reason of this behavior is that as pH of the solution increases (basic nature increases) the adsorbing sites become negatively charged and the negative ions of dye structure do not get loaded on these sites. Conversely when pH



(a) TA (b) MTA

Fig. 8. Percent removal of acid yellow-17 by TA and MTA as a function of particle size.



(a) TA (b) MTA

Fig. 9. Percent removal of acid yellow-17 by TA and MTA as a function of biosorbent dose.

of solution is decreased, the adsorbing sites become positively charged because of the acidic medium and negative ions of the dye are favorably loaded on these sites. So % removal decreases with increase in pH of solution and vice versa.

3.7. Effect of change in particle size of biosorbents on % removal of AY dye

Fig. 8 shows that as the % removal of dye increases the particle size decreases. It is because the surface area is increased and more sites are available when the particle size is smaller, so greater percentage of dye is removed. While if the particle size is greater, the surface area is smaller and lesser number of adsorbing sites is available causing the lower percentage of dye removal.

3.8. Effect of change in biosorbent dose on % removal of AY dye

TA and MTAs were subjected to adsorption process, respectively. Biosorbent dose was varied by keeping the other parameters (shaking time, initial concentration, pH of solution, and particle size) constant. Fig. 9 shows that % removal increased with greater biosorbents dose. The result is very much clear from the fact that greater biosorbent dose provides larger number of adsorbing sites. Therefore, % removal increases with increase in biosorbents dose and vice versa.

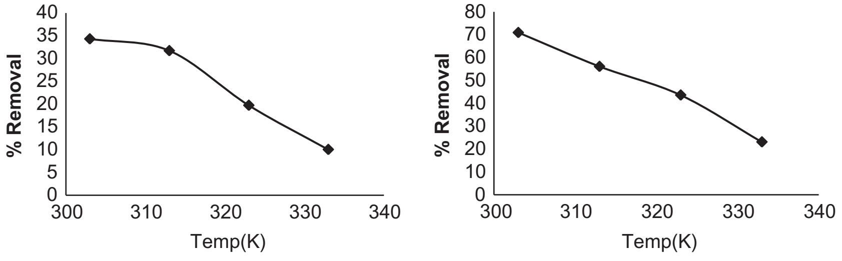
3.9. Effect of change in temperature on % removal of AY dye

Temperature of the solution was varied for this study and the remaining parameters were kept constant. Data for the adsorption of dye by TA and MTAs are given in Fig. 10. The results revealed that the dye removal decreased from 34.67 to 31.87% in the case of TA, while from 74.91 to 58.61% with the temperature increasing from 303 to 310 K in the case of MTA. Since the sorption decreased when temperature rose, therefore, this system was exothermic which is more favorable at lower temperatures rather than at higher temperatures. Biosorption is usually an exothermic process in most of the reported cases, so, it would be expected that decrease in biosorption be caused by an increase in temperature of the dye–biosorbent system.

3.10. Study of isotherms

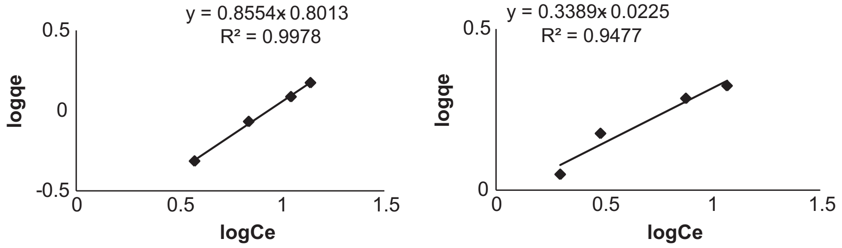
3.10.1. Freundlich isotherm

Assuming the adsorption process as heterogeneous phenomenon, Freundlich gave an exponential form of



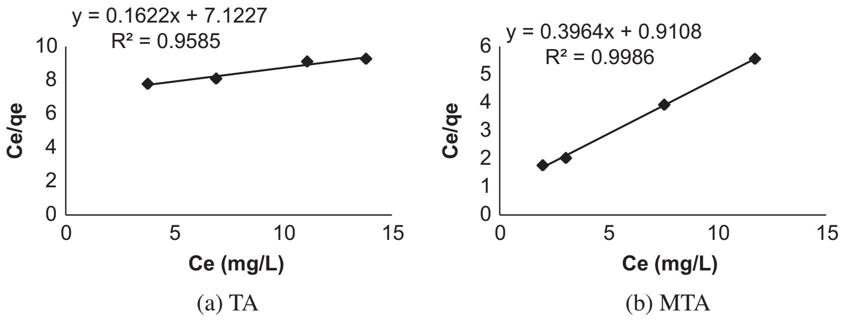
(a) TA (b) MTA

Fig. 10. Effect of temperature on % removal of acid yellow-17 by TA and MTA.



(a) TA (b) MTA

Fig. 11. Freundlich isotherm for the removal of acid yellow-17 by TA and MTA.



(a) TA (b) MTA

Fig. 12. Langmuir isotherm for the removal of acid yellow-17 by TA and MTA.

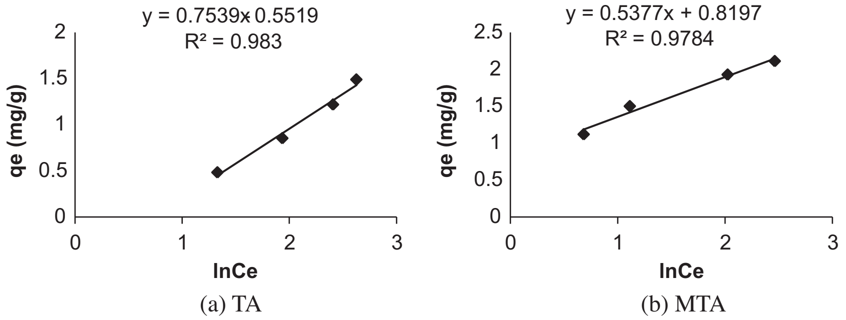
equation which relates q_e (amount of dye adsorbed) with C_e (concentration of dye at equilibrium time). Parameters of Freundlich isotherm for the removal of dye by TA and MTAs are given in tables in Fig. 11. Since the values of n are greater than one, then the adsorption of acid yellow-17 dye is considered favorable on TA as well as MTA. Further, it is obvious the values of co-relation factor for the two graphs suggest that Freundlich isotherm successfully explains the variation of log q_e as a function of log C_e.

3.10.2. Langmuir isotherm

Langmuir isotherm for the removal of acid yellow dye by modified and TA and MTA is given in Fig. 12 and values of C_e/q_e are plotted as a function of C_e (mg/L). In both the cases, values of R_L are zero, which represent the irreversible mode of adsorption of dye on TA and MTA, respectively. From the values of co-relation factor for the Fig. 12, it is obvious that Langmuir isotherm successfully explains the adsorption process as a monolayer formation of dye on the surfaces of biosorbents.

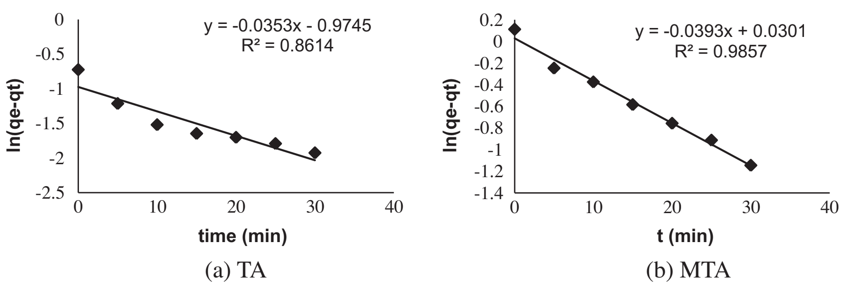
3.10.3. Temkin isotherm

Temkin isotherm helps to study the heat changes associated with adsorption process due to the interaction between dye molecules and adsorbent particles. Parameters for the Temkin isotherm for the adsorption



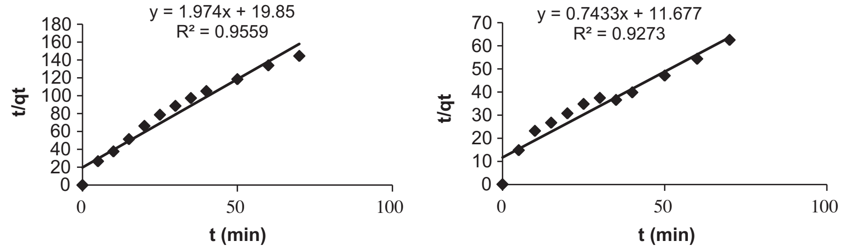
(a) TA (b) MTA

Fig. 13. Temkin isotherm for the removal of acid yellow-17 by TA and MTA.



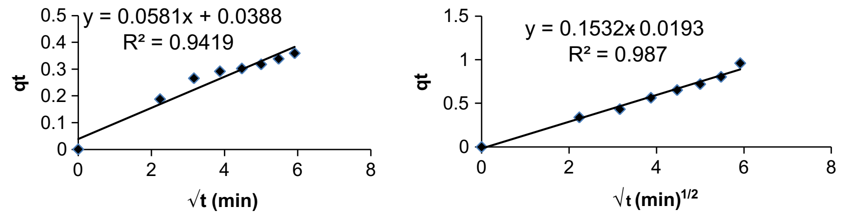
(a) TA (b) MTA

Fig. 14. Pseudo-first-order kinetics model for the removal of acid yellow-17 by TA and MTA.



(a) TA (b) MTA

Fig. 15. Pseudo-second-order kinetics model for the removal of acid yellow-17 by TA and MTA.



(a) TA (b) MTA

Fig. 16. Intra-particle diffusion model for the removal of acid yellow-17 by TA and MTA.

of acid yellow dye-17 by TA and MTAs by the values of q_e and ln C_e are represented in Fig. 13. The R^2 values in figure indicate that Temkin model can be successfully applied to study the heat changes associated with adsorption of acid yellow dye-17 by TA and MTAs.

3.11. Study of kinetics

Rate of the uptake process of acid yellow-17 on TA and MTAs have been investigated by applying pseudo-first-order, pseudo-second-order, and intra-particle diffusion model of kinetics.

3.11.1. Pseudo-first-order kinetics model

Parameters for the pseudo-first-order kinetics of acid yellow dye-17 adsorption by TA and MTA are represented by the graphical representation of values of ln (q_e–q_t) vs. t (min) in Fig. 14. The R^2 values show that pseudo-first-order model explains the adsorption mechanism to a satisfactory level. It is also obvious that q_e (theoretical) are, however, in close relation with the q_e values calculated experimentally from the calibration curve.

3.11.2. Pseudo-second-order kinetics model

The pseudo-second-order kinetics model for the adsorption of acid yellow-17 by TA and MTA is presented in Fig. 15 and are plotted between t/q_t vs. t. The R^2 values show that pseudo-second-order kinetic model explains the adsorption mechanism in more satisfactory way as compared to pseudo-first-order model. In addition, it is also clear that values of q_e calculated theoretically and experimentally from calibration curve are closer as compared to pseudo-first-order data. Here, it is concluded that pseudo-second-order mechanism is more applicable on the adsorption of AY dye by TA and MTA.

3.11.3. Intra-particle diffusion model

This model is applicable for the adsorption processes where there is a possibility of inta-particle diffusion of dye molecules. Parameters of the model for adsorption of dye by TA and MTA are given in Fig. 16 and values of q_t are plotted against the square root values of time. The R^2 values represent that intra-particle diffusion model is also applicable for the adsorption under investigation. It means that there is the possibility of diffusion of dye molecules into the biosorbents molecules. Smaller values of intercept also suggest that intra-particle diffusion most likely may be the mode of adsorption.

4. Conclusion

The major advantages of an adsorption system for water pollution control are less investment in terms of initial cost and land, simple design and easy operation, no effect by toxic substances, and superior removal of organic waste constituents as compared to the conventional biological treatment processes. The adsorption techniques have been found to be useful means for controlling the extent of water pollution due to dyes. *T. Angustata* L. is a material showing the pronounced removal of acid yellow dye from aqueous solutions in alkaline conditions. The capability of the use of *T. Angustata* L. for the removal of acid yellow-17 was examined, including equilibrium and kinetic studies. Biosorption tests were carried out as a function of contact time, biosorbent dose, pH, dye concentration, and temperature. Experiments were performed as a function of initial solution pH, temperature, initial dye concentration, biosorbent dosage, and contact time. The solution pH, temperature, and initial dye concentration played a significant role in affecting the capacity of biosorbent. The further increase in pH over 2.0, temperature over 303 K, and initial dye concentration of 150 mg/L led to a reduction of the biosorption capacity of the biomass. Optimum sorbent dosage was 0.578 g/L of solution with % removal of 89.98 by MTA. The equilibrium between the adsorbate in the solution and on the adsorbent surface was practically achieved in 40 min. Biosorption kinetics was found to follow pseudo-second-order rate expression. Equilibrium biosorption data for acid yellow-17 on *T. Angustata* L. were best represented by Freundlich isotherm. The present study concludes that *T. Angustata* L. could be employed as a low-cost and ecofriendly biosorbent as an alternative to the current expensive methods of removing dyes from textile effluents. The *T. Angustata* L. may be dried and incinerated.

Furthermore, this study indicates that the biosorption capacity of the *T. Angustata* L. is better than many other bio and non-bio adsorbents explored in the literature. Given the facts that *T. Angustata* L. necessitates no pretreatment; it is eco-friendly and low-cost, and that it has a satisfying biosorption capacity, it might well be used in different types of removal activities where textile dyes, phenolics, pesticides, and the like are concerned. Chemical modification of biosorbent with sodium hydroxide further enhances its biosorption capabilities for removing acid yellow dye due to protonation of active binding sites. Isothermal and kinetic modeling shows that chemisorptions occurred during biosorption of dye. Sodium hydroxide-treated *T. Angustata* L. showed a better performance compared to untreated. This study proved that *T. Angustata* L. is an attractive option for the dye removal from dilute industrial effluents.

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