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Removal of acid black 1 by Acacia Concinna; adsorption kinetics, isotherm and thermodynamic study

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Abstract. In the present research, batch adsorption of anionic dye such as Acid Black 1 (AB1) in aqueous solution onto biosorbent Acacia concinna was investigated at room temperature. The effect of various physico-chemical parameters such as contact time, adsorbent dosage, initial dye concentration and temperature on the percentage removal of dye were investigated. Adsorption kinetics was investigated using linear and nonlinear form of pseudo first-order and pseudo-second-order kinetic models but experimental data for adsorption of AB1 dye in aqueous mixture onto biosorbent Acacia concinna was fitted well to pseudo-second order model with maximum value of regression coefficient (0.9995). Linear and nonlinear forms of Langmuir, Freundlich, Tempkin, and Dubinin– Radushkevich (D–R) were used to reveal experimental data but experimental data for adsorption of AB1 dye in aqueous mixture onto biosorbent Acacia concinna fitted well to the Langmuir isotherm model with adsorption capacity 3.21×10^{-4} Adsorption thermodynamic study showed that adsorption of AB1 dye onto adsorbent Acacia concinna was endothermic and spontaneous process. This study revealed that biosorbent Acacia concinna was good biosorbent for removal of dyes from aqueous solution.

Keywords: adsorption; acid black 1; pseudo second order; nonlinear isotherms; three parameter isotherms, acacia concinna

1. Introduction

Water is essential and basic need of human life. It is ranked second after oxygen and life cannot exist without water. Water contamination is the adulteration of natural water bodies by physical, radioactive, chemical or pathogenic microbial constituents. Atoms and molecules are generally considered as chemical water contaminants, which have been exposed to natural water bodies normally by human activities. Most countries endured immense development over the past several era that directed to both progressive and destructive influences to the earth. The emerging environmental issues includes the contamination of environment such as air, soil and water pollution that directly affect the human's life. In the modern era, water pollution is the prevalent problem and its prospective to persuade the health of human being is enormous. Waste water containing dyes and heavy metals effluents is very harmful for environment and human life also (Wawrzkiewicz and Hubick 2012, Renugopal *et al*. 2019). Fabric industry used color heavily because it is the main fascination of fabrics. So the dyeing industry has become an immense source of synthetic dye including effluents that released into water without any treatment causing harmful effects on organisms. The toxicity of synthetic dyes has become a great concern for ecologists. The textile effluent is highly toxic due to the existence of toxic chemicals like naphthol, nitrates, sulphur, vat dyes, chromium compounds, enzymes, soaps and heavy metals including lead, copper, cobalt, arsenic, mercury, cadmium, nickel and some auxiliary chemicals. Some other harmful elements including formaldehydic dye fixative agents, hydrocarbons and non-biodegradable elements makes the water harmful for all life. (Kant 2012).

The effluents of various industries discharged into nearby rivers, lakes, and streams without disbursing care to its influence on living organisms. These effluents contaminated the water and reduced the penetration of sunlight to depth of water and effect the photosynthesis (Malana *et al*. 2010)

Dyeing industries including pulp, rubber, cosmetics, leather, plastics, pharmaceutical and food industries released bases, acids, color, and some other substances as effluents and contaminating the water sources. Dyes are considered the prime contaminant of water (Ong *et al*. 2010, Rattan *et al*. 2008). Every year 100,000 dyes are produced commercially and textile industries utilized more than 7 × 10^5 tons of dyes per year (Carletto *et al*. 2008). Even in low concentration, the dyes are very harmful for aquatic and terrestrial organisms (Gil A. *et al*. 2011). Dyes have damaging effects on gonads, liver, intestine and also cause the irritation to skin with pain and redness. Dyes also effect the gastrointestinal tract and also causes nausea, vomiting and headache (Malana *et al*. 2010). Amongst these concerns, the study on the sequestration of dyes from

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wastewater is significant not only from the fact of selective removal for industrialized usages but also from the ecological aspects. So, it is very significant to eliminate dyes from wastewater.

Different chemical and physical methods, i.e, coagulation and flocculation, Ozonation, photochemical degradation, reduction, oxidation, filtration methods are used to remove dyes from wastewater but these methods are not useful in some cases (Akazdam *et al*. 2017). The physical adsorption technique is known to be an effective procedure for evaluating pollutants from wastewater carried from various industries due to its low cost, non-regeneration of toxic residue, high efficiency and simplicity of design. The cost of physical adsorption procedure mostly relies upon the cost of adsorbent and renewal of adsorbent (Garcia *et al*. 2014, Jawad *et al*. 2020, Jawad *et al*. 2020, Jawad and Abdulhameed 2020). Adsorption is the chief industrial separation method for decontamination of industrial run-off. It is a mass transmission process by which solid material can eliminate soluble components from aqueous solution by means of attraction between dissolved solute on surface of adsorbent. This method has extensive application in elimination of dyes from aqueous waste from industries. Particularly, this technique has greater application in dyeing, leather, textile, and food, paper and plastics, cosmetics, industries in which water treatment is necessary. Adsorption techniques are useful and easy to adopt (Bello *et al*. 2013).

Previously Acid Black 1 dye was removed using pumic stone treated by acid. The results represented that the adsorption data fitted well to pseudo-second order kinetic model (Samarghandi *et al*. 2013). Acid Black 1 dye was also adsorbed by mesoporous carbon synthetic CMK-3 and CMK-3 containing nitrogen functional groups that was treated with ammonia. The results showed that the adsorption of AB1 dye followed pseudo second order kinetics (Peng *et al*. 2014). Activated carbon also used for removal of AB1 dye and experimental data best explained by pseudo-second order kinetic model and Langmuir adsorption isotherm (Hoseinzadeh *et al*. 2012). Cerastoderma lamarcki shells used to adsorb Acid Black 1 dye (Saleh *et al*. 2018).

Activated carbon is most commonly used adsorbent for purification of polluted water because of its larger surface area, high capacity of adsorption, renewable product, high porosity, thermal stability, cost effective material components and presence of various functional groups. Commonly, activated carbon is prepared from nonrenewable starting materials i.e., petroleum coke, lignite and coal that are expensive precursors (Jawad and Abdulhameed, 2020). Activated carbon also prepared, previously, from precursors of various biomass, i.e. corncob, garlic peel, rice husk pellet, sugarcane bagasse, sunflower pith, rice husk, coconut leaf and jatoba barks (Jawad *et al*.2020). However Activated carbon is not useful economically because of its regeneratrion method and high cost preparation methods. Therefore the research interest of researchers moved towards natural and easily available adsorbents (Jawad *et al*. 2020).

The main purpose of this study to reveal adsorption capacity of *Acacia concinna* (Shikakai) fruit for amputation of dyes from wastewater. To the best of our knowledge, *Acacia concinna* has not been utilized for adsorptive removal of AB1 dye from aqueous solution. In present study *Acacia concinna* (Shikakai) pods was used in form of powder and this biosorbent has no substantial marketplace worth. The adsorption effecting parameter, i.e. the influence dye concentration, contact time effect, effect of temperature on removal efficiency and also effect of adsorbent dosage was testified. The rate controlling step and mechanism of adsorption was reported by applying different kinetic models. The adsorption capability of adsorbent Shikakai was also proclaimed by applying different nonlinear and linear isotherm models to experimental data.

2. Experimental, material's and procedures

2.1 Adsorbent

The *Acacia concinna* (Shikakai) fruit was collected in the form of pods. Dust particles were removed by washing the pods and crushed to fine powder. The powdered Shikakai was thoroughly rinsed with tap water to ensure that no sand and dust particle was remained in adsorbent. To prevent the chemical structure destruction by sunlight, the wet fine particles of Shikakai were dried under shade. The distilled water was passed away through the Shikakai powder again to eliminate enduring impurities like unwanted particles and dirt adhered to it. Then *Acacia concinna* was dried in air tight room in shadow. After drying, the powder was sieved to obtained homogeneous sized particles. The biosorbent was saved in air tight packets.

2.2 Adsorbate

Acid Black 1 obtained from Fluka chemicals was used as adsorbate for this experimental work. The 1000 mg/L stock solution was prepared by dissolving 1g of correctly weighed amount of dye in distilled water and working solutions were prepared by diluting this solution. Acid Black 1 is a hair dye having molecular formula of $C_{22}H_{14}N_6Na_2O_9S_2$. It also used in beauty product. Structural formula of AB1 was given below:

Color of Acid Black 1 was shady red to black fine particles and molecular weight was 616.49 g/mol. Corrosive Acid Black 1 was utilized in hair dying agents (Taha *et al*. 2013).

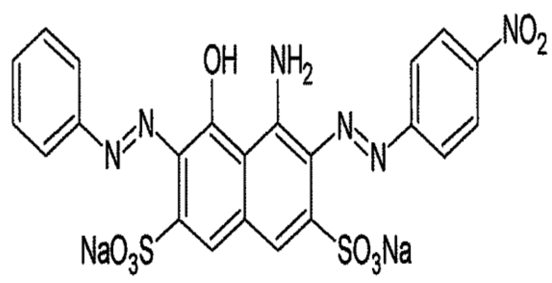

Fig. 1 Structure of AB1

2.3 Adsorption experiment

Batch experiment was carried out for adsorption of AB1 onto *Acacia concinna* adsorbent. At shaking speed of 120 rpm, batch experiment was completed by submersing *Acacia concinna* into the identified volume of dyes. The solution of dye was decanted and UV/VIS spectrophotometer (UV- 2550, SHIMADZU) was used to determine the concentration of dye at wavelength maximum. Concentration of dyes was noted by calibration curve. The adsorption of AB1 on Acacia concinna was calculated by following expression:

$$q_t = \frac{C_o - C_t}{W} \times V \tag{1}$$

where C_o shows the concentration of AB1 before adsorption process and C_t denotes the concentration at time 't'. Similarly, V and W are volume of dye and weight of adsorbent respectively.

3. Results and discussion

3.1 Effect of operating factors

The detail influence of operating endowments onto the removal of dyes is below:

3.1.1 Effect of contact time

The impact of contact time on quantity of dye adsorbed was studied with shaking speed of 120 rpm, 100 mg/L concentration of dye and optimized weight of biosorbent 0.3 g at room temperature and results are shown in Fig. 2 (a). It was detected that percentage exclusion of dye increases quickly with increase in contact time primarily, no markable variation in the percentage elimination was detected after 90 minutes. Consequently, optimum contact time was 90 minutes that was used for further experiments. It indicated that the adsorption of dyes was very fast at initial stages due to the presence of large number of vacant sites available on adsorbent surface. But with the passage of time the availability of active sites become hard to access because of repulsive forces of solute on solid surface.

3.1.2 Effect of biosorbent dosage

The biosorbent weight is a crucial parameter and show significant impact on adsorption of dyes. The influence of biosorbent weight on adsorptive elimination of Acid Black 1 was done by keeping other operating parameters constant i,e, the experiment was done using 100mg/L initial concentration of dye and taking 35ml volume of dye for 90 minutes . Biosorbent weight varied 0.02-0.6 g. It was marked that the removal increases with increase in quantity of *Acacia concinna* and persisted nearly constant after attaining a definite point as represented in Fig. 2(b). This increase is because of increasing biosorbent surface area and accessibility of more active places. The biosorbent, *Acacia concinna* weight optimized was 0.3 g for removal of AB1 dye.

3.1.3 Effect of initial concentration of dye

The maximum color exclusion ability of *Acacia concinna* for Acid Black 1 dye was tested by using variable initial dye concentration and keeping contact time 90 minutes, volume of solution 35 ml, weight of adsorbent 0.3g and stirring speed 120 rpm at ambient temperature and the results are depicted in Fig.2 ©. It was realized that percentage removal decreases by increasing initial dye concentration but the quantity adsorbed per gram increases by increasing concentration of dye. So biosorption was greatly dependent on the initial dye concentration. The amount of dye adsorbed per gram increases with increasing dye concentration due to high concentration gradient that enables the molecules of dyes to move towards the active sites of adsorbent. Similar results were reported by various researchers (Jawad *et al*. 2020). Adsorption capacity of SAMKC increases with increasing Methylene Blue dye concentration. The reason is that higher concentration of Methylene Blue dye provide the greater number of dye molecules to interact with pores of SAMKC (Surip *et al*. 2020).

3.1.4 Effect of temperature on removal efficiency

The impact of temperature on removal of AB1 dye by *Acacia concinna* was also investigated by keeping all other operating parameter constant and results are represented in Fig.2 (d). It was indicated that the removal percentage of dye increases with increasing temperature from 283K to 333K**.** It depicts that high temperature support the removal of AB1 dye from aqueous medium. This increase in adsorption process may be either due to acceleration of certain originally slow adsorption steps or creation of some new active sites on surface of adsorbent and increases the mobility of dye ions which leads to increase in adsorption process. The large number of molecules required sufficient energy to interact with active sites at surface. It reveals that the adsorption of Acid Black 1 dye onto *Acacia concinna* was an endothermic in nature. Similar results are reported by various researchers. The amount adsorbed per gram of CHS-ECH/ZL for Methylene Blue dye show increase with increasing temperature showing endothermic nature of adsorption process. This increase in adsorption capacity may be due to effect of temperature on internal structure of CHS-ECH/ZL that favours the interaction of Methylene Blue molecules into CHS-ECH/ZL (Jawad 2020). The adsorption of RRBR dye molecules increases with elevated temperature may be due to effect of temperature on internal structure of adsorbent CS-TPP/KC surface which leads to facilitate the interaction between adsorbate and adsorbent (Jawad and Abdulhameed 2020).

3.2 Adsorption Kinetics

3.2.1 Pseudo-first order and pseudo-second order kinetics

The linearized form pseudo-first order kinetic model can be represented as (Kumar, 2006; Zafar *et al*. 2019).

$$\log(Q_{e-}Q_t) = \log(Q_e) - (\frac{k1}{2.303})t \tag{2}$$

The nonlinear form of pseudo-first order kinetic model can be represented as

$$Q_t = Q_e(1 - e^{-k_1 t}) \tag{3}$$

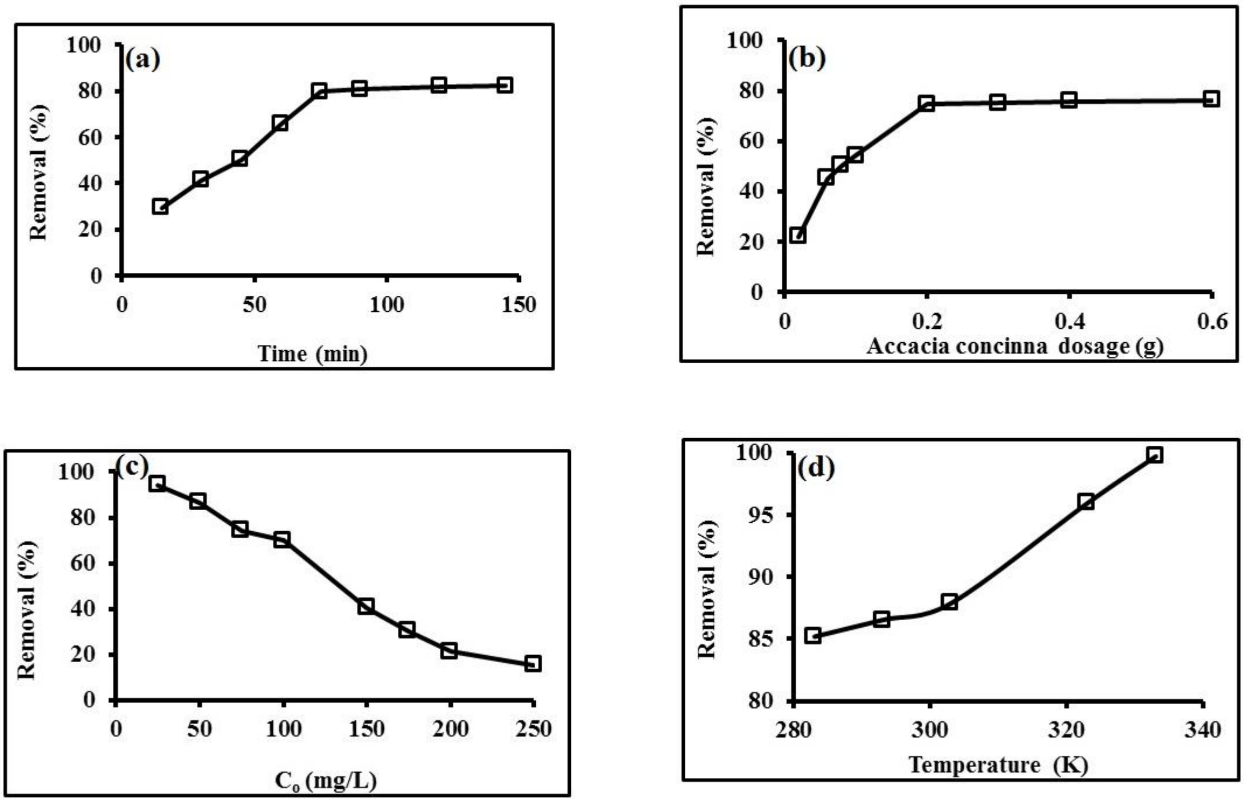

Fig. 2. (a) Effect of contact time on Acid Black 1 removal by *Acacia concinna* biosorbent. (b) Effect of biosorbent (*Acacia concinna*) dosage on removal of Acid Black 1 (c) Effect of dye concentration for removal of Acid Black 1 on *Acacia concinna* biosorbent (d) Effect of Temperature on Acid Black 1dye by *Acacia concinna*.

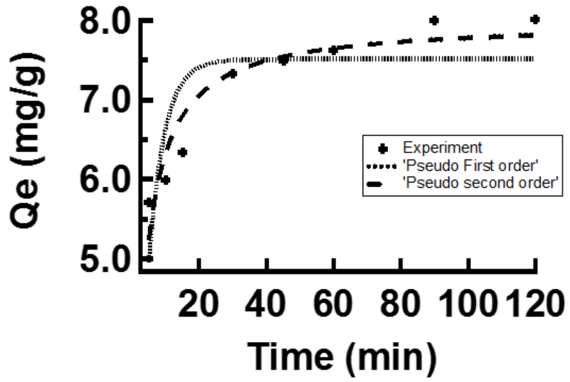

Fig. 3. Nonlinear plot of pseudo-first-order and pseudo-second-order kinetic model for adsorption of AB1 on *Acacia concinna*

Table 1 Pseudo-first-order and pseudo-second-order kinetic parameters for adsorption AB1 in aqueous medium on *Acacia concinna* by nonlinear method

AB1 Dye			
Pseudo-first -order model		Pseudo-second-order model	
Q_e	7.51 ± 0.26	Q_e	7.98 ± 0.19
k_1	0.22 ± 0.04	k_2	0.05 ± 0.009
χ^2	2.29	χ^2	0.65

(Q_e: mg/g; K_1: /min; K_2: g.mg/min)

The pseudo second order can be determined by using this equation (Ho Y.S. 2006; Zafar *et al*. 2019):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} \times t \tag{4}$$

The nonlinear form of pseudo-second order kinetic model can be denoted as

$$Q_t = \frac{K_2 Q_e^2 t}{1 + K_2 Q_e t} \tag{5}$$

where 't' is the time, k_1, (min^{-1}) is the pseudo-first order rate constant, k_2 ($g.mg^{-1}.min^{-1}$) is the rate constant of pseudo second order kinetics. The Q_t and Q_e ($mg. g^{-1}$) are the amount of dye adsorbed from aqueous solution at time and equilibrium respectively. The results shown that the regression value for pseudo-first order kinetic model was not equal to unity and there was great differentiation between experimental and calculated value of Q_e. This showed that pseudo-first order kinetic model was not best fitted for adsorption of AB1 onto *Acacia concinna* adsorbent. The difference between calculated and experimental value of adsorption capacity is not significant and regression value equal to unity for pseudo second order. This showed that adsorption of AB1 on *Acacia concinna* adsorbent followed the pseudo-second order kinetics. The graphical representation for pseudo-first order and pseudo second order is shown in Fig. 4 and results are shown in Table 2. The parameters for nonlinear kinetic models were determined by wave matrix software IGOR PRO 6.1.2 and

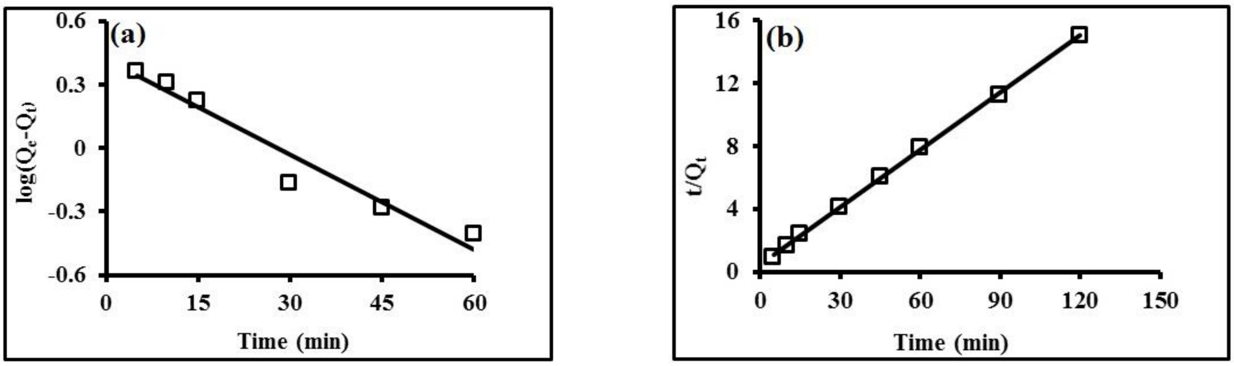

Fig. 4 (a) Pseudo-first-order kinetic for adsorption of AB1 dye on *Acacia concinna* adsorbent (b) pseudo-second-order kinetic model for adsorption of AB1 dye on *Acacia concinna* adsorbent

Table 2 Pseudo-first-order and pseudo-second-order kinetic parameters for adsorption of AB1 onto *Acacia concinna* in aqueous solution by linear method

AB1 Dye			
Pseudo-first -order model		Pseudo-second-order model	
$q_{e\ (Exp.)}$	8.009	$q_{e\ (Exp.)}$	8.009
Q_e	2.67	Q_e	8.25
k_1	0.034	k_2	0.032
R^2	0.951	R^2	0.9995

Table 3 kinetic parameters for adsorption of AB 1 onto *Acacia concinna* in aqueous solution by linear method

Elovich kinetic model		
β (g mg^{-1})	α (mg g^{-1} min^{-1})	R^2
1.24	1.69	0.9686

are given in Table 1 and plot for nonlinear forms are depicted in Fig. 3. Similar results showed by various researchers. The RR120 dye adsorption onto surface of CTSEGDE / FA-25 best fitted to pseudo-second order kinetics due to closeness of R^2 value to unity and furthermore the calculated and experimental values of Q_e are closely related to each other (Jawad *et al*. 2020). Similarly adsorption of RR120 onto surface of CS-GLA/TNC-25 followed pseudo-second order kinetic model. These results may be due to electrostatic interaction between negatively charged sulfonate (ASO3) and positively charged amino (ANH3 +) group of the RR120 dye on adsorbent surface (Jawad *et al*. 2020). Similar results are shown by RO16 dye adsorption onto CS-FA/Fe_3O_4 composite (Jawad *et al*. 2020).

3.2.2 Elovich kinetic model

The Elovich kinetic model is the significant model to interpret the kinetics of observed system. This model described about either the adsorption is chemisorption or physical adsorption. This model best elucidates the chemisorption of the adsorption system. Elovich kinetic model expressed as (Khan *et al*. 2018).

$$Q_t = \frac{1}{\beta}\ln(\alpha.\beta) + \frac{1}{\beta}\ln t \quad (6)$$

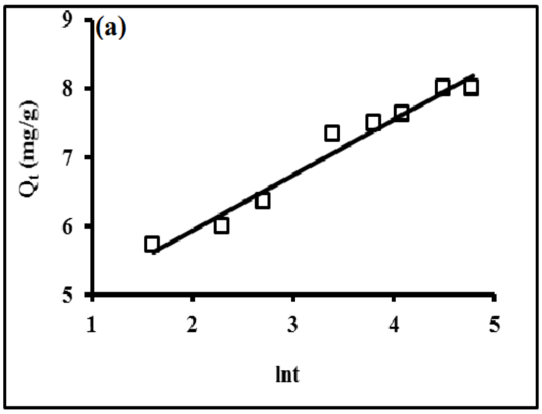

Fig. 5 (a) Elovich kinetic model for AB1 dye adsorbed on *Acacia concinna*

Here, β is correlated to activation energy for chemisorption and extent of surface coverage, α ($mgg^{-1}min^{-1}$) is the Elovich adsorption rate. The plot of Q_t verses lnt is shown in Fig. 5 (a). (Khan *et al*. 2018).

3.4 Adsorption isotherms

For the application of adsorption process on the commercial level, proper quantification of the sorption procedure is required. Sorption equilibrium is necessary for the analysis and design of the sorption process it provides fundamental data of physicochemical method for evaluating the applicability of the process as a unit operation. For this purpose, the experimental data was analyzed using Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich (D-R) adsorption isotherms. Freundlich and Langmuir isotherms were primary adsorption isotherms and are still often applied (Tessema and Alemayehu 2013).

3.4.1. Langmuir adsorption isotherm

The Langmuir isotherm has been used by various workers for the adsorption study of a variety of systems (Langmuir, 1918). Langmuir model supposes homogeneity of the sorbing surface and no interactions between adsorbent species having uniform energies of adsorption onto the surface and no trans-migration of sorbate species in the plane of the surface. The difference in adsorption capacities of two adsorbents for same adsorbate is believed to be largely due to the physicochemical properties of them or the chemistry of solution containing adsorbing species.

The Langmuir adsorption isotherm can be represented as:

$$C_{ads} = \frac{Q_m k_L C_e}{1 + k_L C_e} \quad (7)$$

The Langmuir isotherm can be linearized as:

$$\frac{C_e}{C_{ads}} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (8)$$

where C_e is the concentration of dyes solution (mol/L) at equilibrium and C_{ads} is the amount adsorbed per unit mass onto adsorbent at equilibrium (mol/g). The constant Q_m is monolayer adsorption capacity (mol/g) and K_L (L/mol) is related to the energy of adsorption. In general, Q_m and K_L are functions of pH, ionic media and ionic strength. The value of Q_m for AB1 was computed by linear form of Langmuir isotherm. IGOR Pro 6.1.2, Wave Matrices software was used for the calculation of isotherm parameters while using nonlinear equations. The parameters for nonlinear Langmuir isotherm was represented in Table 4 and plot of nonlinear form were expressed in Fig.7. Similarly the linearized form of Langmuir isotherm model for adsorption of Acid Black 1 dye onto *Acacia concinna* is represented in Fig.6 (a) and attained endowments are given in Table 4. The chi-square value for Langmuir isotherm is 2.65×10^{-12} that indicated that the experimental data best fitted to this isotherm. Smaller the value of chi-square, the best fitted the model.

3.4.2 Freundlich isotherm model

Freundlich isotherm was proposed by Herbert F. Freundlich which is mathematically defined as:

$$C_{ads} = K_f C_e^{1/n} \quad (9)$$

The linearized form of Freundlich isotherm:

$$\log C_{ads} = \log K_f + \frac{1}{n} \log C_e \quad (10)$$

where C_e is concentration of adsorbate at equilibrium in aqueous solution (mol/L) and C_{ads} is sorbed concentration per unit mass of adsorbent (mol/g). 'K_f' and 'n' are Freundlich constants indicating the adsorption capacity and adsorption intensity respectively. The linear form of Freundlich adsorption isotherm for the adsorption of AB1 is represented in Fig.6 (b) and attained parameters are given in Table 4. The experimental data for adsorption of ABI in aqueous mixture onto biosorbent *Acacia concinna* was also subjected to nonlinear form of Freundlich isotherm which is represented in Fig. 7 and attained values of K_f and 'n' are given in Table 4 . The value of n signifies the heterogeneous surface of the anion exchange membrane BII. The values of 'n' ranges from 2-10 indicating good adsorption, 1-2 moderate adsorption and less than one indicates poor adsorption (Subramanyam and Das, 2009).

3.4.3 Tempkin isotherm model

The Tempkin isotherm assumes that the heat of adsorption of all the molecules decrease linearly with the coverage of the molecules due to the adsorbate-adsorbate repulsion and the adsorption of adsorbate is uniformly distributed and that the fall in the heat of adsorption is linear rather than logarithmic (Klaysom *et al*. 2011).Tempkin isotherm in non-linear form described as following equation (Foo and Hameed 2010).

$$Q_e = \frac{RT}{b_T} \ln (A_T) C_e \quad (11)$$

The linearized form of isotherm is shown as (Khandaker *et al*. 2020).

$$Q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \quad (12)$$

where Q_e is amount adsorbed per gram, R, (8.31 J mol.K^{-1}) is gas constant, T , (K) is absolute temperature. The constant b_T is related to the heat of adsorption and A_T is equilibrium binding constant coinciding to the maximum binding energy. Fig. 6 ©. represents the plot of Q_e versus $\ln C_e$ for adsorption of ABI in aqueous mixture onto biosorbent *Acacia concinna*. The values of b_T and A_T were measured from slope and intercept of plot and are given Table 4. The plot of nonlinear Temkin isotherm was shown in Fig. 7 and parameters values are mentioned in Table no.4. The lower value of chi-square and higher value of correlation coefficient depicted that Adsorption of AB1 in aqueous mixture onto biosorbent *Acacia concinna* obeyed the Temkin Isotherm.

3.4.4 Dubinin-Radushkevich model

Dubinin-Radushkevich isotherm also applied to experimental data to determine either the adsorption of Acid Black 1 on *Acacia concinna* is chemisorption or physical adsorption in nature. D-R in non-linear form determined as (Chen *et al*. 2011):

$$C_{ads} = (C_m) \exp(-\beta\varepsilon^2) \quad (13)$$

The linearized form of D-R isotherm (Ociński and Mazur 2020).

$$\ln C_{ads} = \ln C_m - \beta\varepsilon^2 \quad (14)$$

The Polanyi potential ε is described by following equation:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (15)$$

where T is the absolute temperature, and β value, the mean sorption energy (E) can be computed as (Itodo and Itodo, 2010)

$$E = \frac{1}{\sqrt{2\beta}} \quad (16)$$

which is the mean free energy of transfer of one mole of solute from infinity to the surface of adsorbent.

The plots of straight line were obtained by using linear form of D-R isotherm of equation (14) and are presented in Fig. 6d. The values of C_m and β were calculated from

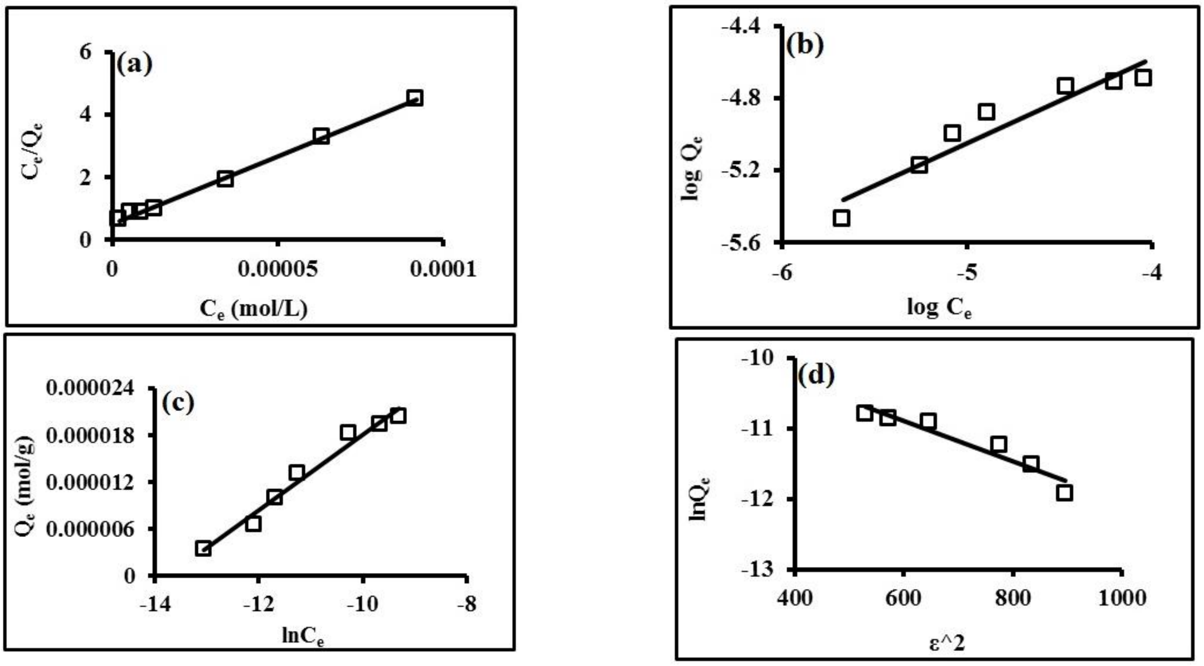

Fig. 6 Linear form of (a) Langmuir, (b) Freundlich, (c) Temkin and (d) D-R isotherms for adsorption of AB1 onto *Acacia concinna* adsorbent

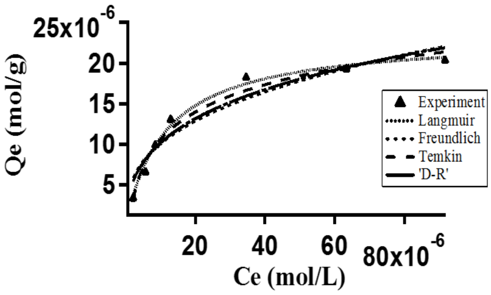

Fig. 7 Nonlinear plot of Langmuir, Freundlich, Temkin and Dubinin Radushkevich isotherms for adsorption of AB1 dye on *Acacia concinna* adsorbent

intercepts and slopes of plot of lnC_{ads} vs ε^2 using a least square fit program and are given in Table 4. The D-R constants (C_m) for adsorption of AB1 in aqueous mixture onto biosorbent *Acacia concinna* was 7.12 $\times 10^{-3}$ mol/g evaluated from intercept of straight lines using least square fit program.

The β values were used for the determination of adsorption free energy (E). The calculated E values for adsorption of ABI onto *Acacia concinna* was 21.24 kJ/mol. These results showed that the chemisorption phenomenon is operative for adsorption of AB1 in aqueous mixture onto biosorbent *Acacia concinna.* The nonlinear plot of D-R adsorption isotherm was represented in Fig. 7 and related constants are represented in Table 4.

3.5 Adsorption thermodynamic study

The feasibility and spontaneity of adsorption process was revealed by thermodynamic study. The change in Gibb's free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) for adsorption of AB1 in aqueous mixture onto biosorbent *Acacia concinna* were calculated from below relationships:

$$\ln Kc = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad (17)$$

Table 4 Isotherm parameters for adsorption of Acid Black 1 dye on *Acacia concinna* by adsorption isotherms

Langmuir adsorption isotherm					
	Q_m (mol/g)	k_L (L/mol)		χ2	R^2
Linear form	3.21×10^{-4}	1.12×10^{5}		_	0.9989
Non-linear form	$2.3\times10^{-5}\pm 1.19\times10^{-6}$	$8.6\times10^{4}\pm 8.61\times10^{-17}$		2.65×10^{-12}	-
Freundlich isotherm					
	k_f (mol/g)	n		χ2	R^2
Linear form	1.89×10^{-3}	2.31		_	0.9107
Non-linear form	$5.9\times10^{-4}\pm 3.5\times10^{-4}$	2.83± 0.47		2.29×10^{-11}	
Temkin isotherm					
	A_T (L/mg)	b_T (KJ/mol)		χ2	R^2
Linear form	1.20×10^{6}	1.24×10^{4}		_	0.9748
Nonl-inear form	$8.8\times10^{5}\pm 1.89\times10^{5}$	$5.04\times10^{5}\pm 3.92\times10^{4}$		6.77×10^{-12}	
Dubinin-Radushkevich isotherm					
	C_m (mol/L)	β (mol^2/J^2)	E (KJ/mol)	χ2	R^2
Linear form	7.12×10^{-3}	1.7×10^{-3}	21.24	_	0.9599
Non-linear form	$9.2\times10^{-5}\pm 2.37\times10^{-5}$	$2.8\times10^{-3}\pm 4.07\times10^{-4}$	13.44	1.78×10^{-11}	

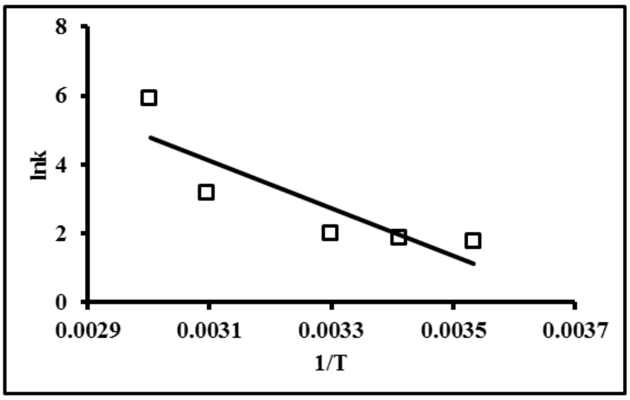

Fig. 8 Plot of 1/T vs lnK for adsorption of Acid Black 1 onto biosorbent *Acacia concinna*

Table 5 Thermodynamic parameters for adsorption of AB1 biosorbent *Acacia concinna*

Dye	T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol/K)
AB1	283	-1.91	57.52	0.21
	293	-4.01		
	303	-6.11		
	323	-10.31		
	333	-12.41		

$$K_c = \frac{C_a}{C_e} \tag{18}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{19}$$

where K_c denotes the distribution coefficient of adsorption, C_a represents the solid phase concentration at equilibrium (mg/L) , C_e depicts equilibrium concentration (mol/L) of dye in solution, R shows general gas constant (8.31 J/mol. K) and T represents absolute temperature (K) respectively. Similarly, ΔG^o, ΔH^o and ΔS^o are the change in Gibb's free energy (kJ/mol), enthalpy (kJ/mol) and entropy (kJ/K.mol) respectively. Fig.8 shows plot of $\ln K_c$ vs 1/T for adsorption of AB1 in aqueous solution onto biosorbent *Acacia concinna*. The change in enthalpy (ΔH^o) and entropy (ΔS^o) measured from slope and intercept of linear Vant Hoff's plot are represented in Table 5. The negative value of Gibb's free energy (ΔG^o) for adsorption of AB1 in aqueous mixture onto biosorbent *Acacia concinna* represents the spontaneity and feasibility of adsorption process. The positive value of enthalpy (ΔH^o) for adsorption of AB1 in aqueous mixture onto biosorbent *Acacia concinna* represented that adsorption process is endothermic. On the other hand, the positive value of entropy (ΔS^o) exhibits the enhancement in randomness at the adsorbate-adsorbent interface during the adsorption process because the increase in temperature may affect the surface of adsorbent and increases the availability of adsorption sites for dye molecules. The increased temperature also facilitates the distribution of dye molecules.

4. Conclusion

The main purpose of this study was to explore the credible use of *Acacia concinna*, a biomass, for removal of acidic dye (AB1) from wastewater material. *Acacia concinna* is very cheap, environmental friendly and easily available adsorbent in low price. The removal of AB1 was studied by different parameters, i.e. contact time effect, biosorbent dosage and adsorbate concentration, temperature using *Acacia concinna* (Shikakai) as adsorbent by batch technique.

- The results showed that the dyes removal increased from 21%-76% as adsorbent dosage increased from 0.02g-0.6g by using 100mg/L initial concentration of dye and taking 35ml volume of dye for 90 minutes.
- The kinetic study disclosed that the removal of AB1 on *Acacia concinna* followed the pseudo second order kinetics with higher regression coefficient (R^2) value 0.9995. Moreover the calculated adsorption capacity, $Q_{m\,(cal)}$(8.2508) is closely related to experimental $Q_{m(exp.)}$ (8.009) value.
- Different nonlinear and linear isotherm models like, Freundlich, Langmuir, Temkin and Dubinin Radushkevich were applied to experimental data that showed the adsorption of AB1 on *Acacia concinna* followed the Langmuir isotherm with correlation coefficient (R^2) value 0.9976. The results showed that the adsorbent *Acacia concinna* have great potential to remove dyes from wastewater.
- The thermodynamic study revealed that the adsorption of Acid Black 1 dye on *Acacia concinna* is spontaneous and endothermic in nature.
- The negative value of Gibb's free energy (ΔG^o) for adsorption of AB1 in aqueous mixture onto biosorbent *Acacia concinna* represents the spontaneity and feasibility of adsorption process. The positive value of enthalpy (ΔH^o), 57.52 for adsorption of AB1 in aqueous mixture onto biosorbent *Acacia concinna* represented that adsorption process is endothermic.
- The positive value of entropy (ΔS^o), 0.21 exhibits the enhancement in randomness at the adsorbate-adsorbent interface during the adsorption process

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