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Research Note

Removal of Novacron black dye from aqueous solutions using low cost agricultural waste: Batch and fixed bed study

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Abstract. The present study deals with the removal of Novacron Black dye with peanut peels biomass, a low cost agricultural waste. The batch mode experiments were performed to compare the biosorption potential of selected biosorbent in its native, glutaraldehyde-treated and immobilized form. Experiments were conducted as a function of pH, biosorbent dose, contact time, initial dye concentration and temperature. Glutaraldehyde-treated biomass exhibited better biosorption capacity as compared to the native and immobilized peanut peels. Maximum biosorption capacity (37.1 mg/g) of Novacron Black dye by peanut peels was observed at pH 2 using 0.05 g biosorbent. Equilibrium data were analyzed by Langmuir, Freundlich and Temkin isotherm models. Langmuir isotherm model fitted very well to the equilibrium data. The kinetic data was modeled using pseudo-first-order, pseudo-second-order and intra-particle diffusion models. Negative values of ΔG° depicted the spontaneous nature of biosorption process. Column studies were performed to optimize the bed height, flow rate and initial dye concentration. The results revealed that the best biosorption was achieved at greater bed heights, lower flow rates and higher initial dye concentrations. Bohrat-Adams model fitted very well to the column data of Novacron Black dye biosorption onto peanut peels biomass.

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1. Introduction

Higher amounts of dyes production and consumption in various industries resulted in the generation of huge volumes of colored wastewater [1]. Dyes are abundantly used for coloring the various products in textile, leather, rubber, paper, plastic, cosmetics, food and pharmaceutical industries [2]. They have complex aromatic molecular structure that makes them quite stable and much difficult to biodegrade [3]. Dye concentration, sometimes less than 1 ppm, is enough to color huge volume of water. It not only affects the aesthetic merit, but also adversely affects the aquatic environment by preventing the penetration of sunlight in water, and reduces photosynthesis process [4]. The carcinogenic and mutagenic nature of synthetic dyes imparts many harmful effects on human being such as kidney dysfunction, damage to the reproductive system, central nervous system, liver and brain. So these dyes must be eradicated from the water textile effluents before their discharge to the natural environments [5].

Extensive research work has been carried out for the treatment of dye containing wastewater. Different technologies like ozonation, chemical oxidation, mem-

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brane separation, irradiation, coagulation and flocculation, catalysis and adsorption have been used for the removal of dyes [6]. The advantages and disadvantages of all these techniques have been extensively reviewed [7]. Among these techniques, adsorption process is considered the most efficient and promising technique for the wastewater treatment [8]. Activated carbon has been proved as an effective dye adsorbent with high adsorption capacities but its large scale application is hampered because of its high operation cost and regeneration problems [9]. So, there is a dire need to find some alternative cheap and abundant biosorbents to remove dyes from water.

Over the last few years, the use of low cost agricultural waste materials has been getting serious attention for the biosorption of dyes and other pollutants. Some of these waste materials for the biosorption of dyes include barely husk [10], hazelnut shells [11], rice husk [4], pine cone [12], jackfruit peel [13], citrus peels [14], neem leaves [15] etc. Low cost and easy availability of these materials make the biosorption process economical for large scale applications. The surface of the agricultural waste materials contains amino, hydroxyl and carboxylic groups which involve in the biosorption of dye molecules. The biosorption capacity of agricultural by-products can be enhanced by various physical and chemical treatments.

This paper reports on the exploitation of different agricultural waste materials for the removal of Novacron Black dye from aqueous solutions. Screening test was conducted to select one biosorbent with maximum biosorption potential among the five agricultural wastes (sugarcane bagasse, peanut peels, corncobs, sun flower and cotton sticks biomass). Batch and column mode experiments were carried out with the selected biosorbent to optimize various process parameters. Batch experiments were conducted to compare the biosorption capacity of selected biomass in its native, modified and immobilized form. The mechanism of biosorption has been studied through kinetic and equilibrium modeling.

2. Experimental

2.1. Chemicals

All the analytical grade chemicals were taken from Sigma-Aldrich Chemical Company (USA) and Merck (Germany).

2.2. Preparation of biosorbent

Peanut peels were collected from Chakwal, Pakistan. The collected biomass was washed with tap water for many times to remove dust and soil. Then it was washed with distilled water and dried in an oven at 60°C for 24 h. It was then crushed into powder and sieved through an Octagon Siever (OCT-DIGITAL 4527-Ol) to a mesh size of 0.250 mm. The sieved biomass was then preserved in an air tight jar for use.

2.3. Pretreatments of biosorbent

The selected biomass was given certain physical and chemical treatments to enhance its biosorption capacity. During physical treatments, autoclaving (biomass was autoclaved at 121°C for 15 min) and boiling (5 g of biomass/100 mL of H_2O boiled for 30 min) were carried out. In chemical modifications, 1 g of the biosorbent was treated with 5% of different acids (HCl, H_2SO_4, HNO_3 and CH_3COOH), alkali (NaOH), surfactants (CTAB, SDS and Triton X-100), chelating agents (PEI, EDTA and glutaraldehyde) and organic solvents (benzene and methanol). Then all the modified biomasses were washed with double distilled water and filtered. The modified biosorbents were dried in oven at 60°C for 24 h and then were grounded [16]. The dried biomasses were stored in air tight bottles.

2.4. Biomass immobilization

The biomass was immobilized by using a matrix of sodium alginate. For this purpose slurry was made by mixing 2 g of sodium alginate in 100 mL water 1g of biosorbent. This slurry was then poured in a burette and was allowed to flow in the form of drops in a 0.1 M solution of $CaCl_2$ contained in a beaker. These drops adopted the shape of beads as they fall into $CaCl_2$ solution. They were filtered and washed with distilled water and stored in 0.05 M solution of $CaCl_2$.

2.5. Preparation of dye solution

Novacron Black dye (λ_{max} 591 nm) used in this experiment was a gift from Swisstex Chemicals, Faisalabad, Pakistan. Stock solution of dye was prepared by dissolving 1 g of dye in distilled water and then making the volume up to 1000 mL with water. It was stored in reagent bottle for further dilutions.

2.6. Batch biosorption studies

The batch experiments were performed by taking 50 mL of aqueous dye solution of a specific concentration in a 250 mL conical flask having known the amount of biomass. The flasks were kept in an orbital shaker (PA 250/25.H) at constant temperature for a period of 2 h at 120 rpm. After shaking, 10 mL of the flask solution was centrifuged at 4000 rpm for 20 min and its absorbance was determined at λ_{max} by UV/Vis spectrophotometer (Shimadzu Brand UV-3000).

2.7. Biosorption equilibrium

Equilibrium experiments were conducted in 250 mL conical flasks with known amount of biosorbent in 50 mL of dye solution. The concentrations of dye solutions used range from 10-200 mg/L. It was agitated

in an orbital shaker for 2 h that is enough time to attain the equilibrium. Then, Langmuir, Freundlich and Temkin isotherm models were applied to the experimental data.

2.8. Biosorption kinetics

Kinetics experiments were carried out at optimum biosorbent dose and pH with variation of shaking time. The samples were withdrawn at different time intervals and analyzed spectrophotometrically. Pseudo-first-order, pseudo-second-order and intra particle diffusion rate equations were applied to the data obtained from contact time experiments to study the kinetics of the biosorption process.

2.9. Biosorption thermodynamics

The experiments were conducted at different temperatures to study the effect of temperature on dye removal at optimum conditions of pH, time, biosorbent dose and dye concentration. Gibbs free energy, enthalpy changes and entropy changes were calculated by using the equation:

$$\Delta G^\circ = -RTlnK_d, \tag{1}$$

$$K_d = q_e/C_e,$$

where K_d is the equilibrium constant, q_e is the biosorption capacity, C_e is the concentration at equilibrium, R is the gas constant (8.314 J $mol^{-1}K^{-1}$), and T is the solution temperature in Kelvin. According to Van't Hoff equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ. \tag{2}$$

The values of ΔH° and ΔS° were determined from the slope and intercept of Van't Hoff graph.

2.10. Column studies

A glass column assembly was used for continuous study. The column has a height of 43 cm with a peristaltic pump and a feed tank for dye solution. The glass column with 20 cm diameter was used in present study. Column was packed with beads of peanut peels biomass up to a certain level and the dye solution was pumped in a down flow mode at a definite flow rate fixed by peristaltic pump. Samples were collected after regular intervals and analyzed spectrophotometrically. The bed height varied between 5 cm (9.6 g), 10 cm (17 g) and 15 cm (21.2 g) by keeping the flow rate and initial dye concentration constant at 1.8 ml/min and 50 mg/L, respectively. Flow rate varied between 1.8 ml/min, 3.6 ml/min and 5.4 ml/min by using optimized bed height and 50 mg/L initial dye concentration. Initial dye concentration was changed between 50 mg/L, 75 mg/L and 100 mg/L at selected bed height and flow rate.

3. Results and discussions

3.1. Screening of biosorbents

Screening test was carried out to select the biosorbent with maximum biosorption capacity for the removal of Novacron Black dye. Five different agricultural wastes (sugarcane bagasse, peanut peels, corncobs, sun flower and cotton sticks biomass) were used for the screening test. The results indicated that among the different biosorbents, peanut peel biomass exhibited maximum potential to adsorb Novacron Black dye from aqueous solutions, so, peanut peels were selected to be used as biosorbent for further study.

3.2. Effect of pretreatments

The biosorption capacity of the biosorbents can be enhanced by performing different chemical and physical treatments. These treatments result in enhancement of surface area, and change the functionality of biosorbents which in turn may lead to the enhancement of biosorption potential. Peanut peel biomass was chemically treated with different acids, alkali, surfactants, chelating agents and organic solvents, and physically the biomass was treated by autoclaving and boiling. The results indicated that pretreatment of peanut peel biomass with glutaraldehyde enhanced its biosorption potential. This might be due to the fact that the treatment of biosorbent with chelating agent might result in the introduction of new functional groups on the surface of biosorbent via direct grafting or polymerization of a monomer [17]. Hence, glutaraldehyde-treated biomass was further used in batch mode experiments.

3.3. Effect of pH

pH of solution plays a very significant role in the biosorption process. It not only affects the properties of the biosorbent material, but also the mechanism of adsorption and dissociation of dye molecules. To investigate the effect of pH, the experiment was conducted by varying the solution pH from 2 to 9, the results of which are presented in Figure 1. The results indicated that the maximum biosorption of dye takes

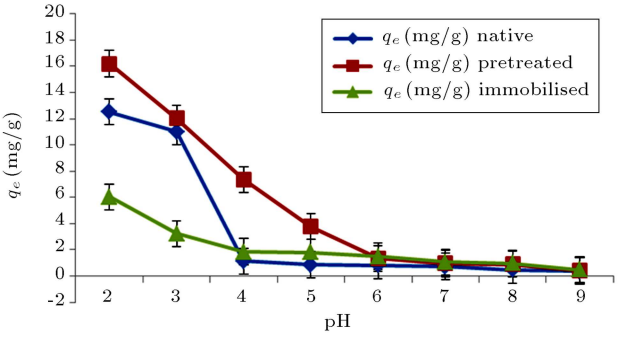

Figure 1. Effect of pH on the biosorption of Novacron Black by peanut peels waste biomass.

place at pH 2 with native, pretreated and immobilized biomass.

Glutaraldehyde-treated biomass showed maximum biosorption potential (16.19 mg/g). This can be attributed to the fact that Novacron Black dye is anionic in nature, and when solution pH decreases, the surface of biosorbent attains positive charge due to the protonation of functional groups, and electrostatic attraction between negatively charged dye molecules and positively charged biosorbent surface leads to the biosorption of dye [4]. As the pH of solution increases, the deprotonation of functional groups takes place and biosorbent surface gets negative charge. The negatively charged biosorbent surface and anionic dye molecules face electrostatic repulsion which results in decrease in biosorption of dye at higher pH range [18]. Similarly Ardejani et al. [19] also examined the effect of pH on removal of dyes and concluded the same trend.

3.4. Effect of biosorbent dose

The biosorbent dose exerts a very prominent effect on the biosorption process. The experiment was carried out to optimize the amount of biosorbent for the maximum removal of Novacron Black dye. The biosorbent dose varied from 0.05-0.3 g and results are shown in Figure 2. The results depict decrease in biosorption of dye with the increase in biosorbent dose. Lesser the biosorbent dose greater is the biosorption capacity, which might be because of aggregation of biosorbent material at higher doses. The aggregation of biosorbent leads to the decrease in surface area and lesser availability of binding sites. The aggregation also leads to the increase in diffusional path length. These facts lead to the decrease in biosorption of dye at higher biosorbent doses [4]. Haq et al. [10] also worked on the biosorption of solar red BA dye by barley husk biomass and found a decrease in biosorption of dye with the increase in biosorbent doses.

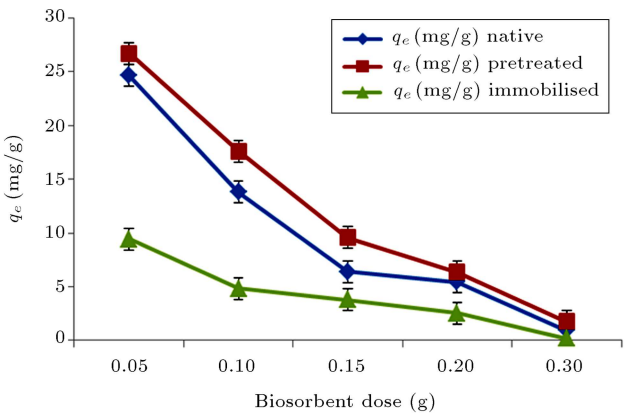

Figure 2. Effect of biosorbent dose on the biosorption of Novacron Black by peanut peels waste biomass.

3.5. Effect of contact time

The effect of agitation time on the removal of Novacron Black dye was investigated to determine the equilibrium time for the dye removal; results are demonstrated in Figure 3. The results revealed that the dye removal increased with increasing agitation time. This increase was very fast in the beginning and then slowed down till equilibrium was attained. The equilibrium was achieved after 120 min. After that time, no remarkable increase in biosorption capacity of biosorbent was observed. In the beginning, a rapid increase was observed in q value that was due to availability of great number of binding sites for dye molecules [20]. The effect of contact time on biosorption of direct dye on palm ash was observed by Ahmad et al. [21] and the biosorption showed a similar behavior. Akar et al. [22] also reported the same trend for biosorption of direct dye and equilibrium was achieved after 40 min.

3.6. Effect of initial dye concentration

The initial dye concentration is an important parameter in the biosorption process. The results of effect of initial dye concentration on biosorption of Novacron Black are given in Figure 4. The results show that the biosorption capacity of biosorbent enhanced at higher

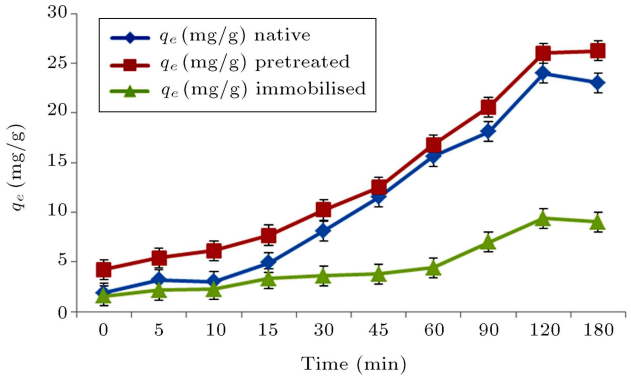

Figure 3. Effect of contact time on the biosorption of Novacron Black by peanut peels waste biomass.

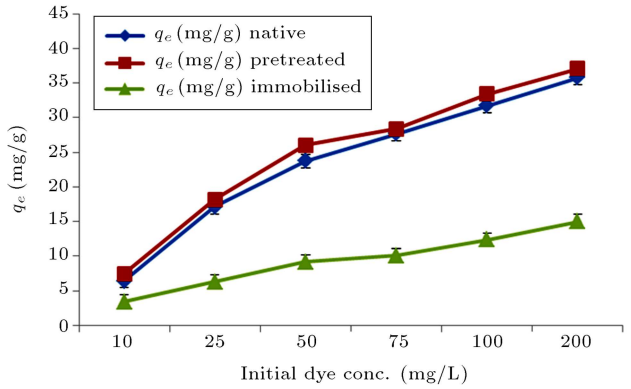

Figure 4. Effect of initial dye concentration on the biosorption of Novacron Black by peanut peels waste biomass.

initial dye concentrations. A high value dye concentration is a significant motivating pull that overcomes all mass transfer resistances of the dye between solid and aqueous phases. An increase in amount of dye also increases the collision among dye and biosorbent ions which multiplies the biosorption potential. Khaled et al. [5] also reported uplift in removal of direct blue on orange peels with an increasing dye amount. Bulut et al. [23] showed that efficiency of biosorption mechanism increased by increasing initial dye concentration. Colak et al. [24] also reported an increase in adsorption sites on the surface of the biosorbent by increasing dye concentration. Similar results have also been reported by Mittal and Gupta [25] for the adsorptive removal of Eriochrome Black T dye.

3.7. Biosorption isotherms

Adsorption data can be analyzed by developing adsorption isotherms. The interaction between adsorbate and biosorbent can be explored by these isotherm models. Three different isotherm models have been employed to explain the biosorption equilibrium data. These include Langmuir, Freundlich and Temkin isotherm models.

3.7.1. Langmuir isotherm model

The biosorption mechanism of dyes can be investigated by applying Langmuir isotherm model [26]. It postulates that the biosorption on the surface of the biosorbent is homogeneous in nature. It suggests that the biosorption of the adsorbate is in the form of monolayer on biosorbent surface. Its linear form is as:

$$\frac{C_e}{q_e} = \frac{1}{q_{m^b}} + \frac{C_e}{q_m}. \tag{3}$$

The Langmuir constants, q_m (maximum biosorption capacity) (mg/g), and b (values for Langmuir constant related to the energy of biosorption) (L/mg) are predicted from the plot between C_e/q_e versus C_e. The values of various Langmuir constants are given in Table 1. The value of coefficient of determination (R^2) defines the fitness of equation to the experimental data. The model is best fitted to the data if value of R^2 is high. The results indicated that Langmuir model is best fitted to the data which reveals that the mechanism of biosorption is chemisorption.

3.7.2. Freundlich isotherm

This isotherm is one of the most primitive known equations that describe the mechanism of adsorption process [27]. It is based on the fact that the surface of the biosorbent is not homogeneous. A logarithmic decline in biosorption energy takes place when occupied binding sites increase. The simple form of the equation is given as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e, \tag{4}$$

Table 1. Comparison of the isotherm parameters for the biosorption of Novacron Black by peanut peels biomass.

Isotherm models	Native	Pretreated	Immobilized
Freundlich			
K_F	9.49	14.56	1.94
n	3.19	4.60	2.27
R^2	0.781	0.861	0.983
Langmuir			
$q_{\max}$ (mg/g)	37.45	37.59	17.45
b	6.48	3.74	23.98
R^2	0.993	0.991	0.981
Temkin			
a (L/g)	0.612	2.03	0.021
b	440.05	545.91	736.65
R^2	0.918	0.850	0.977

where q_e indicates the biosorption capacity (mg/g), K_F is the Freundlich constant related to binding energy, n represents Freundlich exponent related to adsorbent intensity and C_e is the concentration at equilibrium.

The values of K_F and n were obtained by plotting a graph between log q_e and log C_e. The feasibility of the biosorption of dyes on biomass depends upon the value of n and K_f [28]. The values of various Freundlich constants are given in Table 1. The values of n are greater than 1 which describe that the biosorption of Novacron Black onto peanut peels biomass is a favorable physical process.

3.7.3. Temkin isotherm

The basis of this model is that the decline in heat of sorption occurs because of interaction between adsorbate and adsorbent [29]. This decline is not logarithmic but linear as in the case of Freundlich isotherm model.

The model in its linear form is:

$$q_e = B \ln A + B \ln C_e, \tag{5}$$

where $B = RT/b$, T is the absolute temperature in Kelvin, b is Temkin constant and R is the universal gas constant (8.314 J mol^{-1} K^{-1}). A is the equilibrium binding constant and B is corresponding to the heat of sorption. The values of various Temkin constants are given in Table 1. The graph was plotted between q_e (mg/g) and ln C_e to calculate the values of both constants A and B. The dye fitted very well to this model with high values of R^2.

3.8. Biosorption kinetic models

Kinetic studies are essential to optimize the different operating conditions. Chemical and physical properties of the biomass influence not only the rate of biosorption, but also the mechanism of mass transfer. Different

kinetic models have been established to determine the reaction order. Values of various constants present in the models depict the applicability of the model.

3.8.1. Pseudo-first-order kinetic model

The basis of this rate equation is that the change in concentration of dye with respect to time is proportional to the power one [30]. The integral form of the pseudo-first-order model is generally expressed as:

$$\log(q_e - q_t) = \log q_e - K_1 . \frac{t}{2.303}, \tag{6}$$

where q_e and q_t are the biosorption capacity (mg/g) at equilibrium and time t, respectively, K_1 is the rate constant (L/min) and t is the contact time (min). The results indicated that the Novacron Black did not follow this model well.

3.8.2. Pseudo-second-order kinetic model

This model explains the method of biosorption over a wide range of contact time [31]. The differential form of the above model is given by:

$$\frac{dq_t}{d_t} = K_2(q_e - q_t)^2, \tag{7}$$

where K_2 is the rate constant of biosorption process for 2nd order rate law.

After integrating the above equation and applying the boundary equations $t = 0 - t$ and $q_t - 0 - q_t$, Eq. (7) becomes:

$$(\frac{t}{q_t}) = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}, \tag{8}$$

The results of the application of pseudo-second-order kinetic model suggests that Novacron Black adsorption onto peanut peel biomass follows this model well. Safa and Bhatti [4] also reported the fitness of the above model to the direct dyes adsorption on husk of rice. Ozacar and Sengil [32] noted that the biosorption of reactive dye using calcinated alunite also followed this rate law.

3.8.3. Intra particle diffusion

Biosorption process is a several-step mechanism. In the first step, bulk diffusion takes place in which molecules of the adsorbate are transferred to the solid adsorbent. Second step is film diffusion in which boundary layer of the adsorbate diffuses. In the third step, called pore diffusion, the molecules of adsorbate get into pores of the adsorbent. In the final step, chemical reaction takes place between adsorbate and adsorbent molecules. One or more steps may control the adsorption mechanism.

The intra particle rate equation can be written as [33]:

$$q_t = K_{\text{pi}} t^{1/2} + C_i, \tag{9}$$

K_{pi} is the rate constant of intra particle diffusion, and C_i is the intercept from which thickness of boundary layer can be determined. The values of coefficient of determination are quite high for native, immobilized and pretreated biomasses for Novacron Black. So the data is fitted well to this model. Safa and Bhatti [4] reported that the value of R^2 for Direct red-31 is quite high and that of Direct orange-26 is not satisfactory. It plays an important role in biosorption mechanism if the line passes through the origin in a plot between q_t and $t^{1/2}$.

3.9. Thermodynamic studies

The results obtained by performing experiments at different temperatures revealed that q (mg/g) values were improved with raising temperature up to a certain temperature and then showed a decline. Maximum dye removal was achieved at 45°C. The biosorption capacity increased with increase in temperature and then decreased after certain temperature in case of reactive dyes [34]. Bayramoglu and Arica [35] proposed that the movement of the dye molecules increased by increasing temperature. The biosorption of Ramazol black B also showed the same behavior [36]. The values of the standard Gibbs free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated from temperature data and are given in Table 2.

According to Van't Hoff equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ, \tag{10}$$

$$\text{Log}(q/C_e) = -\Delta G^\circ/2.303\ RT = -\Delta H^\circ/2.303\ RT + \Delta S^\circ/2.303\ RT. \tag{11}$$

Table 2. Thermodynamic parameters for the biosorption of Novacron Black on peanut peels biomass.

Temp. (K)	Native			Pretreated			Immobilized		
	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° ($\text{Jmol}^{-1}\text{K}^{-1}$)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° ($\text{Jmol}^{-1}\text{K}^{-1}$)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° ($\text{Jmol}^{-1}\text{K}^{-1}$)
303	-4.06	-85.23	-31.81	-9.13	-13.94	-430.41	0.55	-52.79	-176.58
308	-6.04			-9.05			1.74		
313	-1.35			-2.04			2.95		
318	0.12			-0.003			4.04		
323	0.77			0.51			4.31		
333	2.83			2.70			5.76		

The values of ΔG° and ΔH° were determined from the slope and intercept of Van't Hoff graph. The negative values of ΔG° revealed the spontaneous nature of the process. The negative values of ΔH° showed that the process was exothermic in nature.

3.10. Column studies

As the adsorbate solution passed, the adsorption zone also started moving. The concentration of the column effluent starts rising with the passage of time. This is termed as breakthrough point. So breakthrough time is the time required to reach 50% of initial inlet concentration (C_i).

Breakthrough capacity is calculated by using the relation:

$$\text{Breakthrough capacity} = \frac{\text{breakthrough time (at 50\%)} \; X \text{ flow rate } X \text{ initial dye conc.}}{\text{mass of the adsorbent in the bed}} \quad (12)$$

3.10.1. Effect of bed height

The dye removal efficiency depends upon the amount of the biosorbent present in the column. The experiments were performed at different bed heights of 5, 10 and 15 cm, keeping the flow rate and initial dye concentration constant (1.8 mL/min and 50 mg/L). The graph was plotted between time and ratio of final and initial dye concentration ($C_{\text{out}}/C_{\text{in}}$). It was observed that the breakthrough time was amplified by increasing bed height. It may be because of greater number of adsorption sites available for dye removal. The biosorption capacity was also calculated and was found out to be maximum at 15 cm bed height. This bed height was selected for further experiments. Kiran and Kaushik [37] also reported an increase in dye removal with rise in bed height for dye biosorption. Song et al. [38] investigated that the amount of the methylene blue dye adsorbed increased by increasing adsorbent material in the column. It might be because of greater contact time between dye and adsorbent [38]. Han et al. [39] found out an increase in removal efficiency by increasing bed height for removal of Congo red dye.

3.10.2. Effect of flow rate

For the removal efficiency of biosorbent in continuous treatment process, flow rate is a significant parameter. Flow rate experiments were conducted at 50 mg/L initial dye concentration and 15 cm depth of bed. The breakthrough time and biosorption capacity, both, decreased with increasing flow rate. This was due to lesser contact time between adsorbate and biosorbent, and diffusion limitations at higher flow rates. Han et al. [40] proposed a converse relation between adsorption capacity and flow rate for methylene blue dye. The dye remained to be more in contact at low flow rate. Uddin et al. [41] reported a decrease both in break point time and MB adsorption at higher flow rate. It might be due to low residential time of the dye within the column.

3.10.3. Effect of initial concentration of dye

An important parameter to be studied during continuous mode is the variation in amount of dye. It was observed that the breakthrough time declined as the dye concentration increased from 50 mg/L to 100 mg/L. When amount of dye was enhanced in the solution, the rate of its loading on biosorbent also increased that resulted in a decrease in the length of adsorption zone. The removal capacity also showed a boost by raising dye concentration. The results are in agreement with the work of previous researchers [42,43]. The biosorption capacity obtained from the column study was lower than that of obtained from the batch study for the same initial dye concentrations used. This might be due to the insufficient contact time between the dye molecules and the biosorbent in the column [44]. Column adsorption capacity at various operating conditions of flow rate (ml/min), bed height (cm) and inlet concentration (mg/L) for Novacron Black are given in Table 3.

3.11. Bohart-Adams model

The basis of Bohart-Adams model is that the process of sorption is continuous in nature in which stability is not achieved immediately [45]. The sorption rate

Table 3. Column biosorption capacity at various operating conditions of flow rate (mL/min), bed height (cm) and inlet concentration (mg/L) for Novacron Black on peanut peels biomass.

Inlet concentration (mg/L)	Breakthrough time (50%) (min)	Flow rate (mL/min)	Bed height (cm)	Biosorption capacity (mg/g)
50	18	1.8	15	4.37
75	15	1.8	15	5.46
100	12	1.8	15	5.82
50	9	1.8	10	2.72
50	3	1.8	5	1.22
50	6	3.6	15	2.91
50	3	5.4	15	2.18

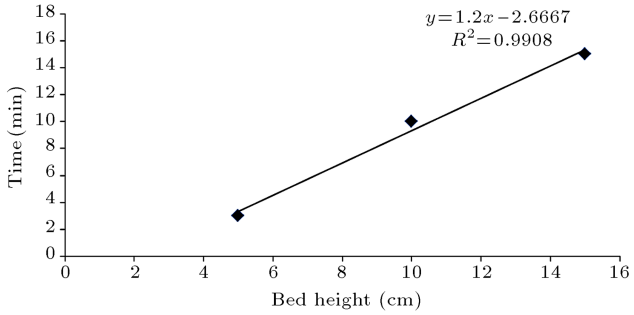

Figure 5. Bohart-Adams model for 50% breakthrough at various bed heights for Novacron Black.

depends upon biosorption capacity that still remains on the biosorbent surface.

This model can be described by the equation:

$$t = \frac{N_o Z}{C_i V} - \frac{1}{K C_i} \ln\left(\frac{C_i}{C_b} - 1\right), \tag{13}$$

where Z is the bed height (cm), N_o is the biosorption capacity of the biosorbent (mg/L), V is the linear velocity (cm/min), K is the rate constant, C_i and C_b are the initial and breakthrough concentrations, respectively. Graph was plotted between bed heights and time under constant experimental conditions for Novacron Black dye and is shown in Figure 5. The values of rate constant and adsorption capacity were found from intercept and slope of the line.

4. Conclusions

The results revealed that peanut peels can be used as efficient biosorbent for the removal of Novacron Black from aqueous solution. The biosorption process was favored at low pH (pH 2), low biosorbent dosage (0.05 g/50 mL dye solution) and high initial dye concentration (200 mg/L). Maximum dye removal with native, pretreated and immobilized biomass was found to be 35.7 mg/g, 37.1 mg/g and 15.2 mg/g, respectively. Langmuir isotherm model was best fitted to the equilibrium data. Thermodynamic parameters revealed the spontaneous and exothermic nature of the biosorption process. Column studies showed the maximum removal of the dye at high bed height, low flow rate and high initial dye concentration. Maximum biosorption capacity of biomass in column model was found to be 5.82 mg/g. Column data of NB obeyed Bohart-Adams model very well as indicated from value of R^2.

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