Senegalia Catechu activated carbon incorporated Ba-alginate composite beads for the removal of Safranine B: modeling studies

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The present investigation depicts the removal of Safranine-Bdye from aqueous solution using senegalia Catechu activated carbon incorporated Ba-alginate composite beads. The alginate beads were synthesized by metal encapsulation technique using $BaSO_4$ as an encapsulating agent. The Safranine-B dye removal efficiency was determined by the modeling equations like Langmuir and Freundlich. The nature of physical, chemical force of attractionbetween the adsorbate vs. adsorbent and feasibility was determined using pseudo order equations of first and second. The progressiveness of the interaction process was predicted by intraparticle diffusion, enthalpy, entropy and Gibbs free energy model equations. Experimentally obtainedoutcomes were implied that the adsorption of Safranine-Bwas feasible for all the parameters used in this study. Furthermore, the predicted diffusion valueswere revealedthat the contact between Safranine-B versus composite beads was well diffused. The surface morphology of virgin and Safranine-B loaded images confirms that the Safranine-B was strappinglybind on outerlayer of the composite. The results of the FTIR spectrum indicatethe Safranine-Bwas intensively attached on the composite surface. The TGA result reveals that the Ba composite bead has predominant temperature bearing nature.

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1. Introduction

The unexpected growth of the world can create huge environmental contaminants which are deteriorating the environment and make as unfavorable. These contaminants are emerging issue for their remediation and removal is challenging for all countries. These contaminants may affect the quality of the water, air, soil and other constituents which persist in the environment as well as the sustainable lifestyle for human beings and other lively hoods. The environmental science and material scienceresearchers and scientists were handled this issue seriously to meet the sustainable lifestyle of the environment. They testedvariety of natural and synthetic materials for the removal of pollution which persist in the environment. This contamination gave alarm to most of the people who live in the contaminated area. Nevertheless, the synthetic organic chemicals have potential totenacious which was resistant to natural biological degradation. To overcome this issue, the selection and picking of predominantnatural materials is importantfor proper remediation of the pollutant. The pollutantscan be infinity in this environment and few of which are identified as emerging pollutants such as organochlorines, polycyclic aromatic hydrocarbons, synthetic dyes, pesticides, polychlorinated biphenyls, wood preservatives, synthetic polymers, pharmaceuticals and personal care products etc... From the above said materials, the synthetic dyes were utilized in

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huge quantity in the industries liketextile, leather, paper, plastic, pharmaceutical, food, cosmetics and dyestuff industries [1]. Generally, synthetic dyes are complex chemical structure, which makes them more toxic able to create residual compounds which is highly resistant to degradation. So, synthetic dyes are more dangerous organic compounds than other material [2]. Moreover, synthetic dyes are commonly toxic, which may act as carcinogenic and mutagenic effects in humans and animals. In water reservoirs, the dyes having prolonged life time which may affect the normal food chain and may cause adverse effects to humans and animals [3]. Therefore, it is essential to remove the synthetic dyes which persist in aqueous bodies to attain a sustainable environment.

In recent years, activated carbon derived from cellulose materials has more attention for pollution removal rather than commercial materials. Activated carbon is tiny particles having high surface area and high attraction over other materials and surface energy. Recently, a vast and unique natural source tree and their constituents are acquiring special attention to scientists for effective adsorption of dyes from the environment [4]. The combination of activated carbon with other natural binding materials were used an emerging new material for pollution adsorption [5]. Various researchers were used activated carbon or modified activated carbon and functionalized activated carbon for the removal contaminants. The chemicals and materials used for functionalizing activated carbon are such as Sulfhydryl [6], thiol[7], amino [8], magnetic [9], alginate [10] and chitosan [11]. This functionalized activated carbon doesrequire separate technology for collecting and recycling of carbon. Hence, still it is a challenging process to recycle and recovery of the collecting and recycling of carbon which possesses an effective adsorption capacity. In some specific conditions, the activated carbon might be susceptible to decrease the filtration ability of membraneor filter separation. Therefore, there may be a coating material is essential to shield their nature [12]. For searching of a suitable coating material, we found that a biopolymer alginate which satisfies the requirement and does not alter the attraction property of the material.

Sodium alginate is biopolymer material which possesses the ability to reduce pollutants. Natural polymers are prone tobind with metals which may produce metal alginate complex beads [13]. The seaweed brown algae was used for synthesize alginate biomaterial. Thepresence of carboxyl group which readily form bond with metal ions for complex structures. Sodium alginate is partially soluble in water and it form gel with 40 to 60°C temperature. The specific character of alginates makes to create a highly stabilized hybrid complex gels. These gels were contributes an assured resultfor decontamination of environment [14, 15].

Senegalia catechu tree stems were collected in the locations of University College of Engineering, Pattukottai. This tree is a deciduous, thorny and it grows up to 50 to 60 feet (15 m) height. This tree found in the countries of south Asia and south EastAsia countries like India, Myanmer, Indonesia and Thailand. Senegalia catechu tree and tree extracted materials can be used as medicine, food, fodder and fire wood. The present study, senegalia Catechu activated carbon were immobilized with alginate biopolymer material and are used for the removal of Safranine-B.

The intentions of this study are to removeSafranine-Bdye from an aqueous medium using a novel Senegalia Catechu activated carbon encapsulated Ba-alginatecomposites. The composite efficiency was evaluated for the adsorptive removal of Safranine-B using the equations like Langmuir and Freundlich, the pseudo kinetic order equations like first, second. The feasibility and diffusion characters were interpreted withintraparticle, entropy, enthalpy, and Gibbs free energy were used. The synthesizedsenegalia Catechu activated carbon encapsulated Baalginatecompositewas analyzed with various analytical methods like Scanning Electron Microscope, Fourier Transform Infrared Spectroscopy, Thermo Gravimetric Analysis and X-ray Diffraction.

2.Materials and methods

2.1. Materials used

All chemicals and reagents used in this study were analytical grades having purity assay of 99.99% and are used without further purification in all experiments. NaOH, HCl, BaSO₄, and

Safranine-B(SF-B)were purchased from Merck India Ltd. Sodium alginate (Purity assay: 99.9%) was purchased from Loba-Chemie Ltd, Mumbai, India. All experiments were carried out with double distilled water.

2.2. Preparation of Senegalia Catechu activated Carbon

The Senegalia catechuactivated carbon was manufactured from the Senegalia catechu tree in the premises of University College of Engineering, Pattukottai.Senegalia catechu tree stems were collected and shortened with the length of 2cm. This stems were dried without sunlight for 15 days to remove the water content. After that, the 2cm stems were allowed to grain in a mill to obtain powder material. This powder is subjected to sieve using desired sizes. The obtained senegalia catechu powder was mixed with 1:1 (18 N)sulphuric acid for 24 hours for complete carbonization of the material. The resultant acid digested materialwas soaked and washed using distilled water until it become free from the acid content (pH=7±0.5). The neutralized carbon then allowed for removing moisture content in hot air oven at 100° C for 24 hours. The resultant carbonwas subjected into300° C in a muffle furnace at for 24 hours to convert into complete carbon. Then the carbon was used for experimental study for no further modification.

2.3. Synthesis of Senegalia Catechu activated Carbonalginate biopolymercomposite

The biopolymer beads were synthesized by taking distilled water of 100 ml in a 250 ml beaker then it placed in hot plate. The distilled water temperature reached in 60° C 1g of Sodium alginate dispersed and stirred well until a transparentnature was obtained. In this context, 1 g of Senegalia Catechu activated carbon added in steady and constant proportion and stirred until get uniform distribution of the carbon. The resultant matrix was poured on drop-wise manner using 10 ml syringe into 100 ml Barium chloride solution (pre-prepared). When the alginate polymer matrix get contact with Barium chloride, the Ba metal can form cross linkage. As a result, beautiful composite balls were obtained. The composite ball beadswere left overnight for curing and attain complete saturation. The remaining barium bath was colorless, this indicate that the complete linkage between alginate and barium metalwith shield membrane. The shield membrane formprevents the leaching of Senegalia Catechu activated carbon from composite beads. On completion of the process, resultant Senegalia Catechu activated Carbon/Ba/alginate polymer composite beads (SCBaPC) were subjected to water wash to remove unbounded barium ions.

2.4. Characterization of SCBaPC

The SCBaPCsurface morphology was determined by scanning electron microscope (SEM) in virgin as well as dye loaded stage. The Fourier transform infrared (FTIR) study was predict the presence of different functional groups in itwith the range of 400-4000 cm⁻¹. Thermal bearing nature of the synthesized SCBaPC beads wasevaluated by Thermo Gravimetric Analysis (TGA). The crystalline nature of the SCBaPC beads was identified with X-Ray Diffraction analysis (XRD).

2.5.Adsorptionprocedure

A Batch mode study was adopted for theremoval of SF-B dye on SCBaPC beads by varying parameters like shaking time (10 min to 90 min), temperature (30° C to 70° C), SF-B concentration (3 mg/L to 21 mg/L), pH (3 to 9) and beads quantity (0.5g to 4 g). The whole batch modeexperiments were carried out with in 50 mL of SF-B dye with agitationof 300 rpm speed with 0.5 g difference of SCBaPCbeads. The absorbance of SF-Bwas identified in initial and finalstage by UV-VIS spectrophotometer. The pH effect was evaluated by adjusting the pH using of 1 M of H₂SO₄ or 1 M NaOH.

3. Results and discussion

3.1. Analytical evidence of SCBaPC beads

3.1.1. FTIR characterization of SCBaPCbeads

Theanalyzed FTIR spectrum of SCBaPC beads was shown in the Figure 1. The peakin the range of frequency peak at 3460 cm⁻¹ represents the presence of moisture [16] or the presence of hydroxyl group [17]. The characteristic peaks assignment of biopolymer-alginate (Figure 1). black line) are as follows: 3460 cm^{-1} and 2970 cm^{-1} (intermolecular bond between O-H stretch), peaks at 2400 cm⁻¹ 1600 cm⁻¹ and 1360 cm⁻¹ shows the presence of six-membered ring and the presence of enol group which was related to the cross-linking reaction by biopolymer [18, 19] another peak at 1110 cm⁻¹ shows CH₃ symmetrical angular deformation [20].



Fig. 1.FTIR spectrum of SCBaPC beads (Black line); SCBaPC beads - SFB (Red line).

Nevertheless, the final state spectrum of SCBaPC beads (Figure 1. red line) shows a broad peak in the range of 3600 cm⁻¹ to 3400 cm⁻¹ show that the N-C stretch (Safranine-B) attached on the beads. Moreover, the peaks at the positions 2380 cm⁻¹ and 1610 cm⁻¹ show that the presence of tertiary amine. Moreover, the before and after adsorption FTIR spectrum was show well deviation of peak intensity, peak position and band width. This trend of change of peaks further confirms that the Safranine-B has toughly adhered on the surface of the SCBaPC beads.

3.1.2. SEM surface analysis

The surfacechange morphology of compositealginate biopolymerbetweenSF-B loaded SCBaPC beads were investigated using Scanning Electron Microscope. Figure 2a shows a porous and uniform layer surface in the SCBaPC beads. While in the Figure 2b, there was a clean and fully covered porous surface in the SF-B loaded stage. These surface changes in non-adsorbed and SF-B adsorbed surface of the composite beads was decided the dye clearly penetrated.



Fig. 2. a)SEM image of SCBaPC beads; (b) SEM image of SCBaPC beads with SF-B.

3.1.3. TGA analysis

Thermal bearing nature of the prepared SCBaPC beads was analyzed with thermogravimetric analysis. The Figure 3 showthe TGA curve of SCBaPC beads. From the figure 3, we saw a steep and slow deterioration against the temperature. Further, a small instabilityfor the range 10 to 200 °C meanwhile the weight loss occurs 15 % ie. 75 to 90 %. This is due to the evaporation of moisture and degradation of biopolymer or oxides of the corresponding minerals. Another fluctuation occurs in the range 230 to 600 °C and weight loss occurs in the range of 20 to 40 % due to the breakage of metal bonds. Beyond the temperature range 800 °C, there was a steep reduction of TG plot indicates that the alginate biopolymerimmobilized as alginate composite which undergone further decomposition and produce no wastage.



Fig. 3. TGA Curve of SCBaPC beads

3.2. Adsorption batch studies

3.2.1. The pH Effect

The working solution pH is highly influence in any adsorption process because solution pH only determines the active surface charge. So, it is mandatory to find out the active sites on the surface of beads[21]. The effect of pH in SF-B dye was assessed by various pH values of 3 to 9 for finding of optimum pH. The obtained experimental results (Figure 4) clearly indicate that the pH 2-6 shows increased percentage of removal of SF-B i.e., 30 % to 97 %. But, the further increase

i.e.,pH 7 to 9, there was unfavorable nature was seen. This results were predicted that the pH- 6 was the most appropriate condition which gave>97% of removal of SF-B. Therefore, pH 6 was chosen as an optimum pH for the adsorption of Safranine-B onto SCBaPCbeads.



Fig.4.The pH Effect forSF-B onto SCBaPC beads.

3.2.2. Effect of SCBaPC quantity

The identification of optimum quantity of SCBaPCwas essential forSF-Bremoval because it mainly alter the nature of adsorption[22]. The surface contact between the SCBaPCvs. Safranine-B has enhanced by varying the quantitywas 0.5 g to 4.0 gwith 0.5 g difference. The figure 5, 0.5 g shows the adsorption efficiency of 64 %. This efficiency increased upto 96% by using 2.0 g of composites. Apart from2.0 g quantity, the percentage does not increasedue to attainment of equilibrium condition in 2.5 to 4.0g, but shows negative effective toSCBAPC beads.



Fig.5.Dose of SCBaPC beads onto SF-B dye.

3.2.3. Time and SF-B concentrationstudies

An adsorption process is highly depends on the shaking time because enough shaking is not avail in an adsorption, the process does not produce an expected results. In the same manner it is very important to identify the feasible concentration of the adsorbent material. The effect of shaking was evaluated by using various SF-B concentrations like 3 mg/L, 6 mg/L, 9mg/L, 12 mg/L, 15 mg/L, 18 mg/Land 21 mg/L in 50ml. By evaluating shaking time, adsorption of SF-B onto SCBaPC beads were originated rapidly with the shaking timeof 10, 20, 30, 40, 50 and 60 minutes but after reaching an equilibrium condition that was not rapid. At the shaking time of 70,

80 and 90 minutes the adsorption of SF-B is not rapid but very slow enhancement was seen in figure 6. From the figure 6, a higher percentage of adsorption was seen in the shaking time of 60 minutes as compared to other contact times. The adsorption percentage of SF-B was calculated from the following equation

$$\operatorname{Removal}(\%) = \frac{C_i - C_f}{C_i} \times 100$$
(1)

where, C_i and C_f are initial concentration and final concentration of SF-B, before and after anadsorption process.



Fig. 6.Effect of shaking time on adsorption of SF-B onto SCBaPC beads.

Using various concentration of SF-B, 15 mg/L would give higher adsorption percentage of >96 % as compared to the other concentrations of SF-B.This experimental result concluded that the 15 mg/L of SF-B has an optimum concentration for the adsorption of SF-B onto SCBaPC beads.

3.2.4. Effect of Temperature

Temperature is generally influence all types adsorption process and which canmodify an equilibrium capacity of particular sorbate material. The evaluation of effect of temperature of SF-B onto composite beads was done using the temperature range of 30 to 70 °C. By evaluating various temperatures 40 °Cwas produces >96 % of adsorption than other temperatures in Figure 7.



Fig. 7.Effect of temperature on adsorption of SF-B onto SCBaPC beads.

Beyond this temperature the percentage of adsorption get reduces steeply which means that above this temperature the adsorption process is not feasible. This reduction of adsorption was attributed due to reduction of the physical forces of attraction between SF-B and composite beads. From the observation of experiments, the optimum temperature of adsorption of SF-B has been chosen as 40 °C onto composite beads.

3.2.5. Isotherm studies

In this present study, well-known isotherm equations like Langmuir and Freundlich models were used for the simulation of experimental data's. The Freundlich isotherm model is based on the concept of the process was involved in a heterogeneous layer [23]. The mathematical form of the Freundlich equation is as follows,

Non-linear form of Freundlich equation

$$q_{e} = K_{F} C_{e}^{1/nF}$$
⁽²⁾

The linearized form Freundlich equation

$$\log q_e = \log(K_F) + \frac{1}{nF} \log(C_e)$$
(3)

where, q_e is the amount of SF-B optimized at equilibrium (mg/g), C_e is an equilibrium concentration of the SF-B (mg/L), K_F is a Freundlich constant related to the optimized capacity of the SCBaPC beads ((mg/g)(L/mg)^{1/n}) and 1/n is optimized intensity (Figure 8).

The n values of the Freundlich constant predicts the feasibility of the adsorption process ie. n-value lies between 2 < n < 10, 1 < n < 2 and <1 represents a good, difficult and poor progression adsorption, respectively[24]. The experimental data determined in this study were presented in the Table 1. From the table 1, the value of n was lying between 2 to 8 (Table 1), which represents the progression of good adsorption of SF-B.



Fig. 8. Freundlich isotherm on adsorption of SF-B onto SCBaPC beads.

The Langmuir isotherm model used as the assumption of an adsorption proceeds in homogeneous sites, which involved in an intramolecular bonding on composite beadsurface and attains a specific site occupation. There is no extension of adsorption found on the occupied site of the composite beadmaterial. This indicates that an adsorption process is progressed in a monolayer process [25]. The mathematical form of the Langmuir equation is written as,

Non-linear form of Langmuir equation

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \tag{4}$$

The linearized form of Langmuir equation

$$\frac{C_e}{q_e} = \frac{1}{q_m}C_e + \frac{1}{K_a q_m}$$
⁽⁵⁾

where $q_e (mg/g)$ and $C_e (mg/L)$ are the amount of SF-B optimized per unit mass of alginate biopolymerimmobilized alginate and un-optimized concentration in solution, q_m is the maximum amount of SF-B optimized per unit mass of alginate biopolymerimmobilized alginate at complete monolayer on the surface bound, and $K_a (L/mg)$ is a constant related to the affinity of the binding sites. Various forms of Freundlich and Langmuir equations were presented in the Table 1.

Isotherm		Concentration (mg/L)							
Isotherm		3	6	9	12	15	18	21	
Langmuir 1	$q_m(mgg^{-1})$	0.0651	0.1512	0.2729	0.1977	0.3017	0.3613	0.4297	
	$K_a(Lmg^{-1})$	2.9203	2.1518	2.7198	2.991	9.1079	5.9693	5.7294	
	r ²	0.9977	0.9953	0.9937	0.9955	0.9977	0.9991	0.9996	
Langmuir 2	$q_m(mgg^{-1})$	0.0656	0.1545	0.2822	0.2046	0.3101	0.3658	0.43238	
	$K_a(Lmg^{-1})$	2.9632	2.2624	3.0875	3.5191	12.3796	6.6702	6.0752	
	r ²	0.9800	0.9420	0.8942	0.8769	0.8403	0.9263	0.9604	
	$q_m(mgg^{-1})$	0.1935	0.342	0.8273	0.6711	3.4143	2.315	2.5531	
Langmuir 3	$K_a(Lmg^{-1})$	0.3387	0.4489	0.3373	0.301	0.0899	0.1571	0.1688	
	r ²	0.9911	0.9694	0.9367	0.9174	0.8718	0.9404	0.9676	
Langmuir 4	$q_m(mgg^{-1})$	0.1959	0.3552	0.8902	0.7362	3.8937	2.4579	2.6359	
	$K_a(Lmg^{-1})$	0.336	0.4369	0.3186	0.2793	0.0798	0.1489	0.164	
	r ²	0.9911	0.9694	0.9367	0.9174	0.8718	0.9404	0.9676	
Freundlich	1/n	0.5094	0.3861	0.2517	0.1992	0.0906	0.1059	0.1001	
	$K_F(mgg^{-1})(Lg^{-1})$	2.1254	2.4545	2.5463	2.6843	2.7854	2.8966	3.1233	
	r ²	0.9549	0.9451	0.9106	0.8956	0.8903	0.9102	0.9095	

Table 1. Isotherm parameters for the removal of SF-B.

The correlation coefficient of Langmuir isotherm equation shows the r^2 value is>0.9996, which derived from the linearized form (Figure 9a). This closest unity value represent the experimental data's were best fitted with Langmuir model isotherm equation rather than Freundlich model r^2 value is >0.9549 (Figure 8). The other forms of linearized Langmuir equations show the r^2 value 0.9800, 0.9911, 0.9911 for Langmuir-2 (Figure 9b), Langmuir-3 (Figure 9c) and Langmuir-4 (Figure 9d) isotherm equations respectively (Table 1). This concluded that Langmuir model isotherm was dominant as compared to the Freundlich model isotherm.



Fig.9.(a) Langmuir isotherm-1 on adsorption of SF-B onto SCBaPC beads;(b) Langmuir isotherm-2 on adsorption of SF-B onto SCBaPC beads;(c) Langmuir isotherm-3 on adsorption of SF-B onto SCBaPC beads;(d) Langmuir isotherm-4 on adsorption of SF-B onto SCBaPC beads

3.2.5. Kinetic studies

In this study, the Lagergren's pseudo-first order and pseudo-second order linearized kinetic equations were fitted with experimental data. The pseudo-first order equation was used as an assumption of the rate of change of adsorption SF-B with time may lead to changes in the uptake capacity of SCBaPC beads. This phenomenon was directly proportional to the saturation of the concentration difference and the amount of solid uptake with time[26]. The mathematical form of pseudo-first order equation is written as

$$\log(q_{e} - q) = \log(q_{e}) - \frac{K_{1}t}{2.303}$$
(6)

where, K_1 is the pseudo first order adsorption at constant, q_e is the amount of SF-B optimized on the composite equilibrium (mg/g), q_t is the amount of SF-B optimized on at any time t (mg/g).



Fig. 10.Pseudo-First order plot on adsorption of SF-B onto SCBaPC beads.

The experimental data were also tested by the pseudo-secondorder kinetic model, which is used in an assumption of the rate limiting step involves chemical forces of attraction and reaches over in the whole adsorption processes[27]. The mathematical expression of the equation is

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$
(7)

where, K_2 is the pseudo second order adsorption rate constant, q_e is the amount of SF-B optimized at equilibrium (mg/g), q_e^2 is the pseudo-second order rate constant (g/mg/min).



Fig. 11.Pseudo-Second order plot on adsorption of SF-B onto SCBaPC beads.

The pseudo-second order rate constant was obtained by plotting a graph between $t/q_t vs. t$, from which a straight line was obtained. Using a linear fit of the plot, q_e and k_2 were calculated with the slope and intercept. Various forms of linearized equations of kinetic model were presented in the Table 2.

C_0	Pseudo-first order kinetics			Pseudo second order kinetics			
	K ₁	q _e	r ²	q _e exp.	K ₂	q _e cal	r ²
3	0.0061	0.1464	0.6427	0.69	6.5588	0.0421	0.9995
6	0.0102	0.0311	0.7384	1.59	2.1239	0.0550	0.9951
9	0.0103	0.0950	0.8698	2.94	1.5023	0.0460	0.9666
12	0.0088	0.0475	0.8579	3.69	2.8420	0.0225	0.9645
15	0.0049	0.2039	0.9136	4.49	8.5648	0.0124	0.9964
18	0.0032	0.2930	0.8948	5.64	3.1696	0.0226	0.9735
21	0.0023	0.3829	0.8844	6.26	3.0478	0.0291	0.9864

Table 2.Kinetic parameters for the removal of SF-B.

According to the correlation coefficient value (r^2) of pseudo-second orderis > 0.9995 (Figure 11)and pseudo-first order is 0.9136(Figure 10)which was from the Table 2. This correlation coefficient value clearly indicates that the adsorption of SF-B onto SCBaPCbeads was influenced by chemical forces rather than physical forces[28, 29]

3.2.6. Diffusion mechanism

The investigation of the diffusion mechanism of the process is using an intraparticle diffusion model equation. The mechanism of diffusion of adsorption process is generally involved in three steps as (i) The transfer of the mass across the boundary layer involved in external film of the liquid surrounding on outside of the particle, (ii) the surface adsorption proceeds in a specific site on the surface (internal or external) and the energy level will depend on which type of the binding process (physical or chemical) involved (iii) The diffusion of SF-Bmolecules on adsorption site either by a pore diffusion process through the liquid filled pores or by a solid surface diffusion mechanism[30]. The rate controlling step involved in any adsorption process should be one or any combination of which can be the rate-controlling mechanism [31]. The mathematical expression of the intraparticle diffusion equation is given as

$$q_t = K_{id} t^{1/2} + C$$
 (8)

where, k_{id} is an intraparticle diffusion rate constant and C is intercept.

C ₀ (mg/g)	$k_{id}(mg/g.s^{1/2})$	C (mg/g)	r ²
3	-0.0001	0.0276	0.7297
6	-0.0007	0.0546	0.8151
9	-0.0013	0.0763	0.9100
12	-0.0008	0.0449	0.8931
15	-0.0007	0.0356	0.9249
18	-0.0006	0.0356	0.9063
21	-0.0005	0.0352	0.8924

Table 3. Intraparticle diffusion parameters for the removal of SF-B.

The adsorption experiment may involve in multi-linear step, which is two linearized steps influence the adsorption process. The first linear line indicated that an instant adsorption of Safranine-B, which produces an initiation step of the process in steep line[32]. At this line represents the intra-particle diffusion is a major diffusion and moreover other line indicates that

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there are some boundary layer adsorptionmay also be involved in controlling step of the adsorption of SF-B onto compositebeads. The predicted intraparticle diffusion parameters were presented in the Table 3.

3.2.7. Thermodynamic studies

The prediction of thermal effect of adsorption process using thermodynamic equations may contribute for the deliberation of whole process mechanism and the changes in the permanently attributed energies that are associated with that process. The parameters used in this study, such as change in Gibbs energy (ΔG^0), change in enthalpy (ΔH^0) and change in entropy (ΔS^0), are predicted using the following equations [33].

$$K_{id} = \frac{q_e}{C_e} \tag{9}$$

$$\Delta G^0 = -RT \ln K_{id} \tag{10}$$

$$\ln K_{id} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$
(11)

where, K_{id} is the distribution coefficient, T is the temperature and R is gas constant (8.3145 J/mol/K).



Fig. 12. Van't Hoff plot on adsorption of SF-B onto SCBaPC beads.

By plotting a graph between ln $K_{id}vs$. T using the linear regression analysis, the thermodynamic parameters of ΔG^0 , ΔS^0 and ΔH^0 were calculated by using Vant Hoff's plot in Figure 12.

T (°C)	ΔG^0 (KJ/mol)	ΔH ⁰ (KJ/mol)	ΔS^0 (KJ/mol/K)
30	-0.72	0.07	31.98
40	-0.79		
50	-0.96		
60	-1.00		
70	-1.19		

Table 4. Thermodynamic parameters for the removal of SF-B.

Experimentally calculated and predicted thermodynamic parameter values were presented in Table 4. From the table, the ΔG^0 shows a negative value which implies that the process is spontaneous in nature[34, 35]. The enhancement of higher negative values indicates the quantity of dye uptake from the equilibrium value may be increased. The ΔH^0 provides a positive value which confirms the endothermic nature [36]of adsorption process and there was a possibility of strong interaction between the SF-B and SCBaPC beads[37]. The ΔS^0 value confirms the involvement of good affinity for the adsorption of SF-B onto compositebeads.

4. Conclusion

The analytical study of the present investigation of FTIR and SEM studies were shownconsiderabledifference in before and after adsorption states of the SCBaPC beads. The TGA implies that the material has high temperature with standing capacity. The effect of pH on SCBaPC beads results the optimum pH value of 6. The Langmuir isotherm was the best suitable model compared to the Freundlich isotherm model. The Freundlich isotherm feasibility was investigated with the n value, and the value lies between $2 \le n \le 10$. The kinetic studies follow the pseudo-second order model rather than pseudo-first order model and intraparticle diffusion shows two segments of straight lines.

The thermodynamic function of ΔG^0 provides negative value that implies that the process is unprompted of progression. The ΔH^0 provides a positive value that confirms the endothermic nature of adsorption and positive ΔS^0 value confirms the involvement of good affinity for the adsorption of SF-B towards SCBaPC beads. All parameters obtained from this experiment shows that the Safranine-B adsorption was strongly favors onto the SCBaPCcompositebeads.

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