Research Article

Isothermal, Kinetic and Thermodynamic Studies for the Adsorptive Removal of Pregabalin from Aqueous Solution as Well as Industrial Effluents

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Abstract

Sesame seed cake powder (SSCP) in its carbonized form has been utilized in the adsorption of pregabalin from the solutions in aqueous state as well as industrial effluents. Characterization of the adsorbent has been carried out by using FTIR, PXRD and HRSEM. Effect of pH, initial drug concentration, adsorbent dosage, contact time and temperature and the impact on the uptake of the drug was investigated and optimized. The optimized conditions for removal of pregabalin are a pH of 7, initial drug concentration of 10 mg/L, adsorbent dosage of 0.2g, contact time of 50 min and temperature as 25 ^{o}C. Kinetic studies for the bio-sorption of the chosen formulation inferred that the process follows pseudo second order kinetics with R^2 value of 0.999 and K_2 of 0.765 g/mg min. Isothermal studies indicated that Langmuir isotherm fits suitable for the adsorptive removal of pregabalin. With the highest adsorption capacity of 2.04 mg/g, the adsorbent showed an appreciable removal 84.4% of pregabalin from the aqueous solutions. Applicability of the adsorbent towards industrial effluents has also been performed and the results indicated that the adsorbent and the process fits perfect for the efficient treatment of the effluent.

Keywords: Bio-sorption, Pregabalin, Langmuir isotherms Pseudo second order kinetics, Freundlich isotherm and Temkin isotherm

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Introduction

Pregabalin with chemical formula $C_8H_{17}NO_2$ is sold under the brand name Lyrica and is extensively used as a medicine in the treatment of neuropathic pain, epilepsy, generalized anxiety disorder, fibromyalgia, and restless leg syndrome [1-4]. Adverse effects of the medication are as that of common CNS depressants [5] and also include dizziness, drowsiness, hypotension, first degree heart block, hypertension, suicidal thoughts, pancreatitis and abnormal walking [6]. Although the medication has a wide spread application in disorder/ disease treatment, the adverse effects are frightening too. Hence, treatment of effluents containing the pharmaceutical product is imperative. Various waste water treatment methods like photolytic degradation, ion exchange, precipitation and adsorption are widely used for the removal of heavy metals, organic pollutants as well as pharmaceutically active compounds(PhAs). Removal of pollutants using adsorption technique gained great prominence in the present-day scenario. Adsorptive removal of pharmaceutically active compounds like analgesics, antibiotics, antidepressants, contraceptives, growth regulators, pain killers, and tranquilizers [7-9] has been carried out by using nanomaterials, other synthetic frameworks and activated carbons. In view of high cost of these materials, recently biomass, byproducts of industrial processes and even solid waste from various industries have been used as adsorbents in their native as well as carbonized forms for waste water treatment. Almond husk, sunflower stalks, saw dust, rice husk and spent grain have been reported to be utilized for the removal of pharmaceutical contaminants from waste water [10]. These materials are found to be cost effective in comparison with various bio adsorbents reported till date.

In the present study, sesame seed cake powder (SSCP), a byproduct from edible oil industry in its carbonized form was chosen for the elimination of pregabalin from aqueous solutions and industrial effluents employing the adsorption technique.

Experimental

Chemicals and instruments used

Throughout the experimentation, analytical grade chemicals and double distilled water is used.

Preparation of adsorbent

Sesame seed cake was purchased from the local market. Sesame seed cake is the residual solid material obtained subsequent to oil production. The seed cake being a hard mass, fist crushed and finely ground into powder using a ball mill. A fine powder with invariable particle size is the result. The powder thus obtained is sun dried for three days to eliminate any trace of oil left over. Such sample was washed thoroughly by the help of distilled water, dried in an oven and stored for further experimentation. The sample is then placed in a crucible and heated until the substance got completely carbonized and stored in air tight containers to avoid any contamination.

Preparation of pregabalin solution

Pregabalin aqueous solution has been prepared by dissolving 100 mg of the pure drug sample in 100 mL and standardized [11]. A series of varying concentrated solutions were prepared from the stock solution.

Equipment

Bruker advanced D2 PHASER instrument has been used for XRD analysis. Perkin Elmer Spectrum Two has been used for FTIR analysis. Residual concentration of the drug in the filtrate as well standardization of the drug concentration has been carried out by using Waters system (E2695) HPLC instrument. Scanning Electron Microscope images were obtained by using TESCAN VEGA3 LMU model instrument.

Batch adsorption studies

A series of bottles containing varying quantities of SSCP with the adsorbate (pregabalin solution), batch experimentation was carried out at optimum pH by continuous agitation. The adsorbent was agitated with 50 mL of 10 mg/L solution of the formulation. The pH of the solution was adjusted by using 0.1N hydrochloric acid and/or 0.1N sodium hydroxide until the pH was stabilized. This mixture is continuously and thoroughly agitated until equilibrium is attained. Concentration of the formulation was measured by HPLC using UV detector at 254 nm after filtering the mixture through a Whatmann No.1 filter paper.

Results and Discussion

Characterization of adsorbent

Sesame seed cake powder was found to have a surface area of 488 m^2 g^{-1}. The obtained value is higher when compared to other carbons. SEM images have clearly showed that the chosen adsorbent has fine porosity with a particle size in the range 3-7 µm (**Figure 1**). The adsorption capacity of carbon is affected by the chemical structure of the surface, which are of carbon- oxygen functional groups. In many instances, the functional groups which are responsible for the surface activity are phenolic, carboxyl, carbonyl, hydroxyl and lactones groups. FTIR spectrum of the adsorbent which was obtained also confirms the same (**Figure 2**). The complete IR spectral data is provided as supplementary file (Figure S1 and S2). From the FTIR spectra it is inferred that SSCP contained 3008 cm^{-1} (trans =C–H stretch), 2954 (–CH_3 asymmetrical stretch), 2922 and 2853 (symmetrical and asymmetrical stretching of –CH_2), 1743 (–C=O stretch), 1654 (cis –C=C stretch), 1463 (–CH_2 bending), 1417 (cis =C–H bending), 1377 (–CH_3 bending), 1237 (–C–O stretch), 1160 (–C–O stretch; –CH_2 bending), 1120 (–C–O stretch), 1098 (–C–O stretch), 1032 (–C–O stretch), 965 (trans –CH=CH– bending out of plane), 871 (=CH_2 wagging), and 722 $cm^{-}1$. From these values it may be inferred that the adsorbent is carbon sufficient. Powder X-ray diffraction studies were done for the adsorbent to assess the bulk chemical composition and physical state. From the results, it was found that the adsorbent chosen is of completely amorphous in nature (**Figure 3**).

All the results obtained from the optimization of the process are presented in **Table 1**. Effect of each of the parameters is graphically represented in Figure S3-S7 in supplementary file.

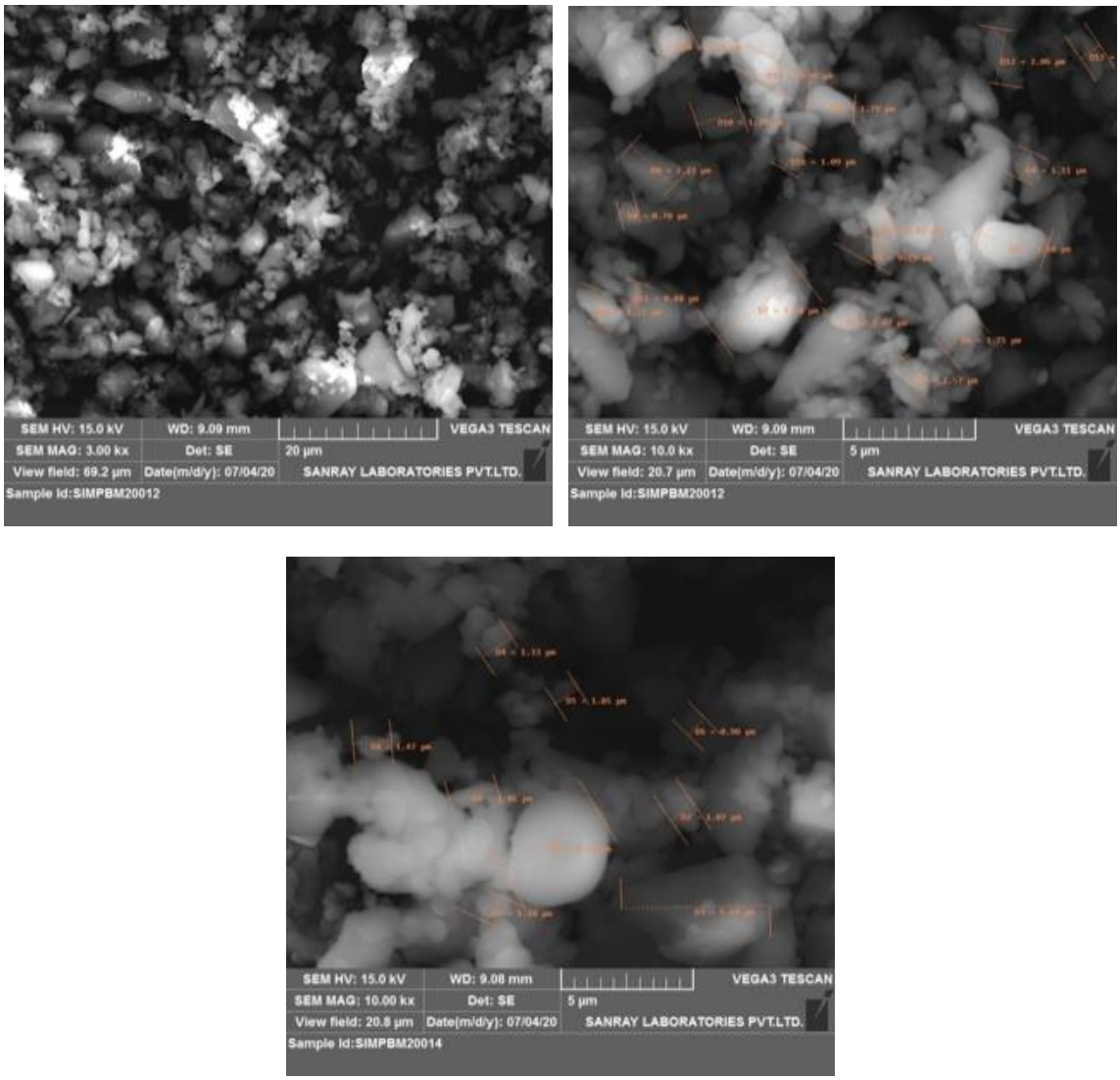

Figure 1 SEM images of SSCP (a) Cavities in the structure (b) Showing the particle size in the range 3-7µm (c) Interior morphology of the adsorbent showing large number of cavities

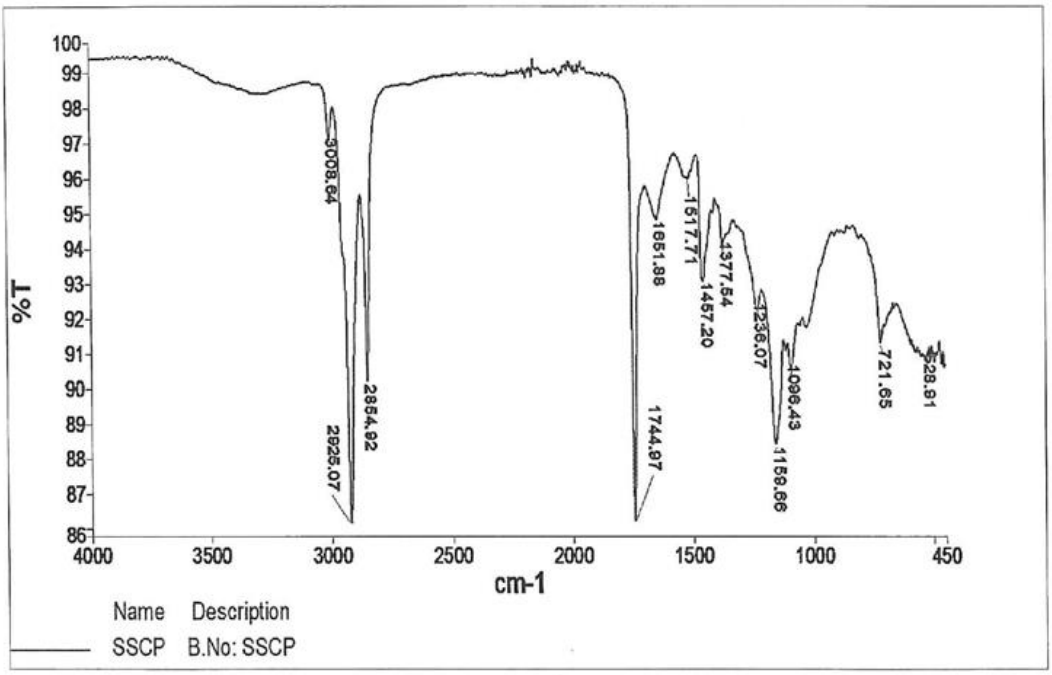

Figure 2 Fourier transform infrared analysis of SSCP powder

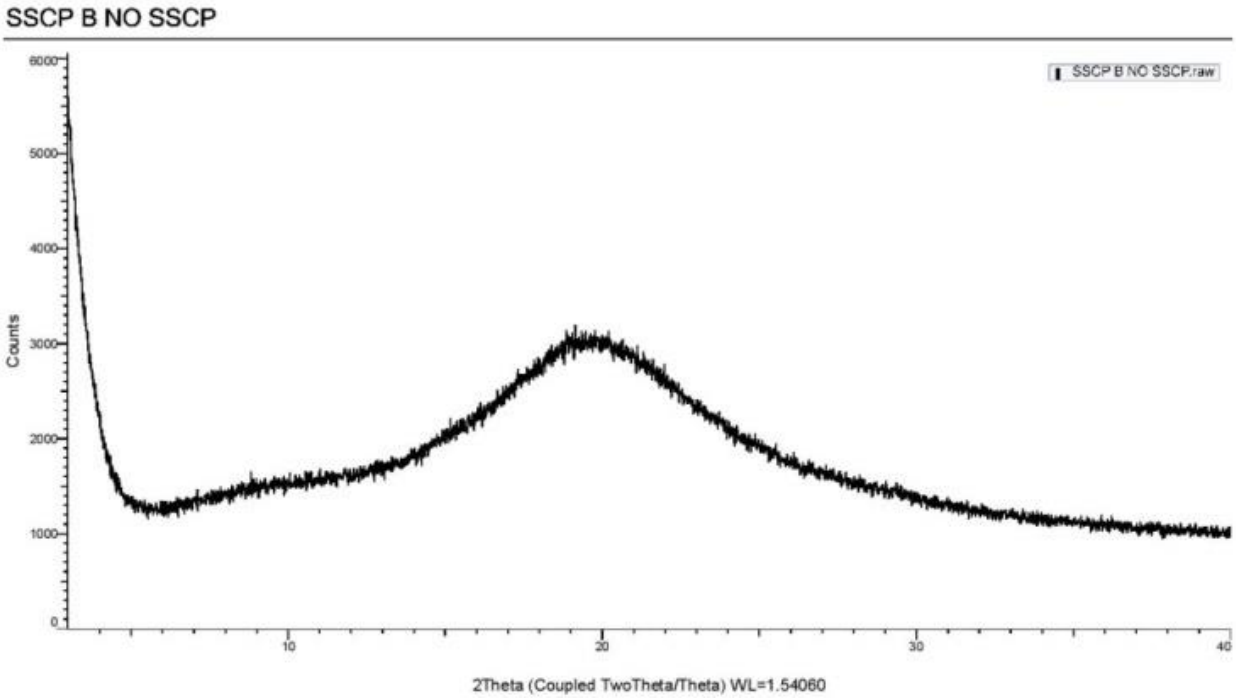

Figure 3 PXRD report of SSCP powder

S.No	Parameter	SSCP
1	pH	7
2	Temperature in (degree Celsius)	25
3	Adsorbent dosage (g)	0.2
4	Initial drug concentration (mg/L)	10
5	Contact time (min)	50
6	Q_{max} (mg/g)	2.5

Table 1 Optimization parameters for the adsorption of pregabalin

Adsorption studies

Adsorption of pregabalin on a low cost material such as SSCP was studied as a function of pH, adsorbent dosage, contact time, drug concentration and temperature. The adsorption data was fitted to different isotherms of adsorption.

Since pH infers the degree of ionization, speciation of adsorbate and surface charge of the adsorbent, effect of pH on the removal of the drug plays a vital role. From the results it was found that, dissociation of the drug molecule was found and lead to weak forces of attraction between adsorbent and adsorbate at pH greater than seven. Experimental results indicated that the removal of pregabalin is found to be effective at pH value of 7 and hence optimum pH for the removal of pregabalin using SSCP has been fixed at 7.

To fix the optimum adsorbent dosage for the removal of pregabalin using SSCP, a series of experiments were conducted. The experimentation was carried out by taking 0.1-1.0 g of the adsorbent for batch studies. The results showed that 0.2 g of SSCP is the optimum adsorbent dosage for the its removal.

In investigating the optimum contact time between SSCP and pregabalin for its uptake, a series of experimentation was carried out by maintaining the pH and adsorbent dosage at the optimum values and by varying the time of contact. From such series of experiments equilibrium time required for the effective uptake of pregabalin by the adsorbent was established and found to be 50 minutes.

A set of bottles containing each 0.2 of SSCP and solution of pregabalin in varying concentrations (10-90 mg/L). These mixtures were agitated for 50 min at a pH of 7. After the equilibration time, concentration of pregabalin in the filtrate was determined. As the concentration of the drug increases, the adsorption efficiency of the adsorbent decreased as the number of active adsorption sites decreases. 10 mg L^{-1} of the pregabalin was found to be the optimum drug concentration for its adsorptive removal.

Maintaining all the other parameters like pH, adsorbent dosage, time of contact, initial drug concentration at their respective optimum values, experimentation was conducted to investigate the optimum reaction temperature. Experimental results showed that at 27^{o}C of temperature pregabalin has been efficiently removed from aqueous solution. The percentage removal of the drug decreased as the temperature is increased.

Isothermal studies

Mechanism of adsorption of the drug on SSCP can be assessed by using isothermal modelling. For the purpose, Temkin, Langmuir and Freundlisch adsorption isotherm models have been used. The mathematical expressions for these three adsorption isotherms are as follows:

Langmuir adsorption isotherm

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

Freundlich adsorption isotherm

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

Temkin isotherm

$$Q_e = \left(\frac{RT}{b}\right) \ln K_T + \left(\frac{RT}{b}\right) \ln C_e$$

Results obtained from the isothermal modelling studies is presented in **Table 2**. These results indicated that adsorption of pregabalin from aqueous solution fit to Langmuir adsorption isotherm (**Figure 4**). In Langmuir adsorption isotherm, q_m is sorption capacity and K sorption energy and are related to Langmuir constants. Q_e is the amount of pregabalin adsorbed per unit weight of adsorbent and C_e is the equilibrium concentration in mgL^{-1}. A plot of Ce/ Q_e vs C_e was drawn and correlation coefficient from the graph was found to be 0.9993. This substantiates the fitness of the isotherm for the study. Q_{max} obtained for the removal of the formulation using SSCP was found to be 1.789 mg/g. This value coincides with the value computed theoretically.

Freundlich and Temkin isotherms (**Figures 5** and **6**) were also plotted and showed that with a relatively lower correlation coefficient these two models are not suitable to explain the adsorption of the pregabalin on SSCP.

Table 2 Adsorption isotherm characteristics for the removal of pregabalin using SSCP

S. No	Adsorbent	Langmuir Adsorption isotherm			Freundlich Adsorption isotherm			Temkin adsorption isotherm		
		q_{max}	K	R^2	K_F	1/n	R^2	B	A	R^2
1	SSCP	1.978	33.59	0.9993	1.433	0.0911	0.368	0.1214	24009	0.29

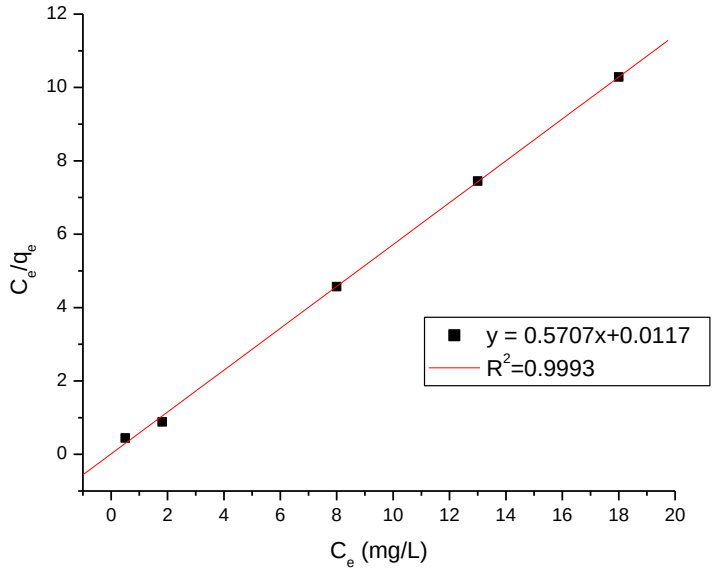

Figure 4 Adsorption isotherm for the adsorption of pregabalin on SSCP- Langmuir model

Thermodynamic studies

In order to ascertain the spontaneity of an adsorption process, entropy and energy data must be considered. The practical application of any process is governed by the thermodynamic parameters [12-13]. To compute the thermodynamic parameters for the present adsorption system, the amount of pregabalin adsorbed at equilibrium at

different temperatures of 25, 35 and 45 °C were examined. From the following equation, thermodynamic parameters like standard enthalpy change (ΔH), standard free energy change (ΔG) and standard entropy change (ΔS) were computed. The results computed were presented in **Table 3**.

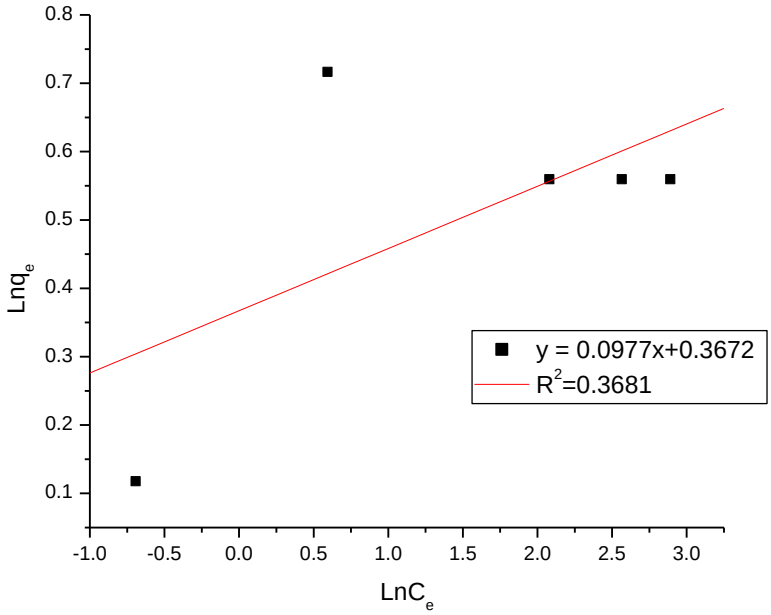

Figure 5 Adsorption isotherm for the adsorption of pregabalin on SSCP- Freundlsich model

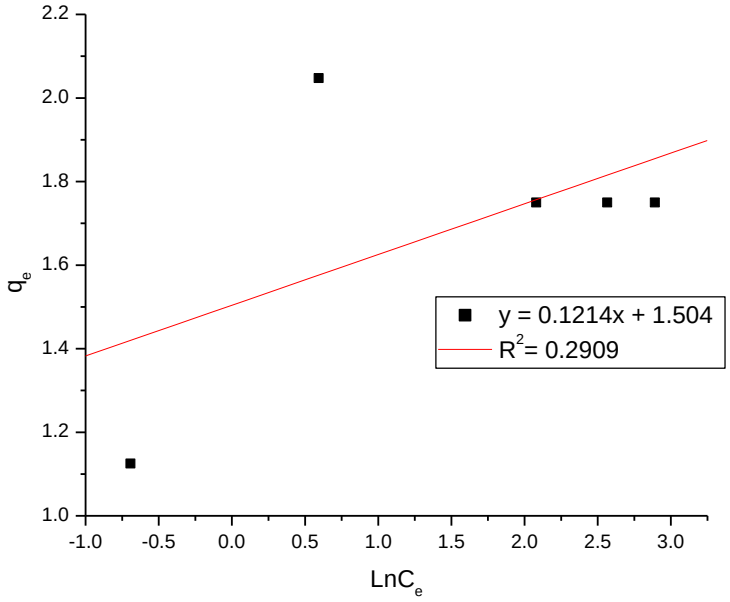

Figure 6 Temkin adsorption isotherm for the adsorption of pregabalin on SSCP

$$\ln b = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

$$\Delta G = -RT \ln b$$

Here, R is universal gas constant (2cal/ mol/K), T is temperature and b is equilibrium constant or Langmuir constant. ΔH and ΔS can be calculated from a plot drawn between ln b vs 1/T.

As the values of ΔH (-4.5 Kcal /mol) obtained is less than 10 Kcal/ mol, it indicates that the adsorption of pregabalin on SSCP is an exothermic process and physisorptive by nature. Negative value of ΔG (-1.9 Kcal/mol) infers that this adsorption process is feasible and spontaneous in nature. The decrease in the degrees of randomness of the adsorbed species is a result of the negative value of ΔS (-8.2 cal/mol/K).

Table 3 Thermodynamic parameters for the adsorption of pregabalin using SSCP

S.No	Thermodynamic parameter	Value obtained
1	Standard enthalpy change (ΔH)	-4.5 Kcal/mol
2	Standard entropy change (ΔG)	-1.99 Kcal / mol
3	Standard Gibbs free energy (ΔS)	-8.2 cal/ mol K

Studies on reaction kinetics

Reaction kinetics of adsorption of pregabalin on SSCP has been studied and presented here. Lagargren's pseudo-first order kinetics, pseudo-second order models are the widely used among the many kinetic models developed.
Pseudo-first order rate expression is given as

$$\mathrm{Log}\,(q_e - q) = \log q_e - \frac{kt}{2.303}$$

Where k is the adsorption constant, q_e is the amount of solute adsorbed at equilibrium by the unit weight of adsorbent and q is the amount of solute adsorbed at a given time.
Mathematical expression for pseudo second order rate equation is

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$$

The results of kinetic analysis were presented in **Table 4**. A plot is drawn by taking time on x-axis and corresponding t/q_t values on y-axis. Pseudo second order rate constant was determined from the lope and intercept obtained plots. Here, q_t and q_e are the sorption quantity at time t and equilibrium respectively, k is the rate constant of the process.

It is inferred from the results that the sorption of pregabalin using the chosen adsorbent followed pseudo second order kinetics the same was presented in **Figure 7**. Correlation coefficient (R^2) for the process was found greater than 0.993 indicating the fitness of the model for the present process. The rate constant value of pseudo second order reaction was found to be 0.756 min^{-1}.

Table 4 Kinetic parameters for the adsorption of pregabalin using SSCP

S.No	Adsorbent	Pseudo first order kinetics			pseudo second order kinetics		
		q_e	K_1	R^2	q_e	K_2	R^2
1	SSCP	3.759	0.522	0.512	1.975	0.765	0.999

Applicability towards real samples

A known volume of the industrial effluent obtained from Revin Laboratories LTd, containing pregabalin has been taken and carried for batch adsorption procedure at the optimized conditions as mentioned above. Triplicate analysis has been performed to assess the suitability for the method for the real samples. From the results it was found that the chosen adsorbent effectively adsorbed the drug up to 92% from the effluent. From the results of triplicate experimentation, the standard deviation is found to 0.4% and variance is found be 0.6%. These values were well within the prescribed limits.

Comparison with activated charcoal

To the best of the knowledge of the authors, it was found that for the first time the chosen adsorbents as well as the drug have been used by the authors. Hence to compare and to validate the results obtained, activated charcoal has been used and at the optimized conditions the adsorption efficiency has been investigated and found that 88% of the drug has been removed using activated charcoal with Q_{max} of 2.01 mg/g. The maximum adsorption is found to be equal for both activated charcoal as well as the three adsorbents of the study. Though, both the adsorbents showed similar results, as SSCP is economical, abundant and biologically derived which are ecofriendly hence the adsorbents are found to be superior to activated charcoal.

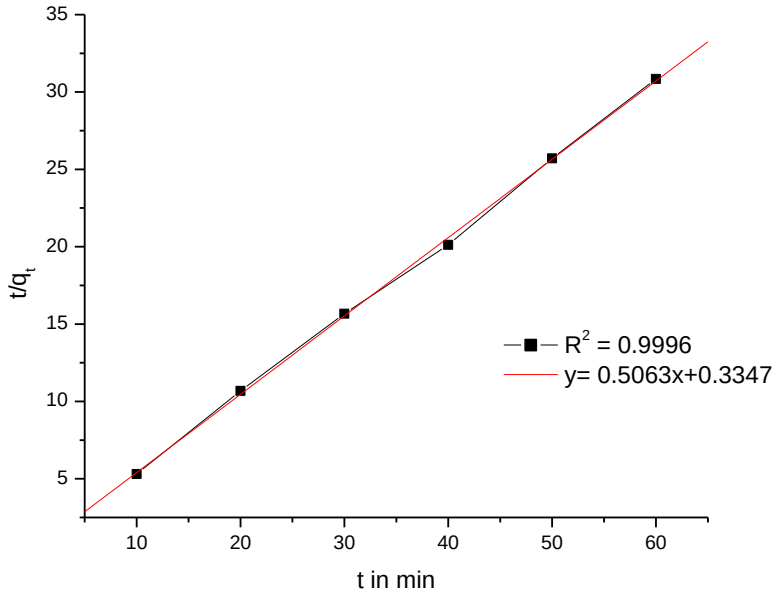

Figure 7 Psuedo second order kinetics for the adsorption of pregabalin on SSCP

Conclusions

The batch adsorption experiments carried out in the present study provides significant information on the adsorptive removal of pregabalin. These studies inferred that SSCP is an effective adsorbent for the removal of pregabalin. Adsorption of pregabalin using SSCP, bio-adsorbent was optimized at a pH of 7, initial drug concentration of 10 mg/L, adsorbent dosage 0.2 g, contact time of 50 minutes and temperature of 27ºC. In the present investigation, pseudo second order kinetics of reaction rates fits perfect. Langmuir adsorption isotherm perfectly fits the adsorption of the pharmaceutical formulation using the adsorbent. Using the bio-sorbents 84.4% of the formulation was effectively removed from aqueous solutions. Thermodynamic data of the present study explained that the adsorption of pregabalin on SSCP is feasible, exothermic and spontaneous in nature.

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