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Byproducts from the edible oil industry as potential adsorbent for the removal of Pregabalin from aqueous solution

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Temkin isotherm

Abstract

Removal of Pregabalin from aqueous solution as well as industrial effluent using a new, efficient and cost-effective activated carbon derived from groundnut seed cake powder (GNSCP) and coconut cake powder (CCP) has been presented in this study. Experimentation has been carried out by optimizing various parameters such as pH, contact time, dosage, temperature and initial drug concentration using a batch adsorption model. Surface texture and morphology of the activated carbons have been analyzed by HR SEM; Characterization of the adsorbents has been carried out using FTIR and PXRD. Bio-sorption of Pregabalin using GNSCP and CCP followed pseudo-second-order kinetics. Langmuir adsorption isotherm suits the best for the present study. Thermodynamic studies showed that the adsorption of the drug onto the chosen adsorbents is a spontaneous and feasible process. The maximum adsorption capacity for the uptake of Pregabalin by GNSCP was found to be 9.71 mg/g and with CCP 9.83 mg/g. Suitability of the adsorbents for the treatment of industrial effluent has also been carried out and found to have 98 % removal of the drug from the effluent.

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INTRODUCTION

Since decades, water resources available on earth are being contaminated by toxic chemicals such as heavy metals, organic pollutants and even pharmaceutical products from various industries (Calisto and Esteves, 2009). Besides industrial pollution man-made activities, urbanization is also responsible for water contamination. Significant research has been focused on the treatment of wastewater contaminated by pharmaceutically active compounds (PhAcS). NSAID's, antibiotics, antiepileptic, and pain killers are some among the PhAcS that have been found to contaminate water. These compounds cannot be easily removed due to their resistance and persistence to the aquatic environment (Guler and Ford, 2010). Existing methods like flocculation, filtration and activated sludge (Brodin *et al.*, 2013; Ternes *et al.*, 2004) were found to be ineffective in the treatment of pharmaceutical industrial effluents. Methods like nano-filtration,

ultrafiltration reverse osmosis (Rivera-Utrilla *et al.*, 2013; Comerton and Andrews, 2007), polyamide film nanofiltration (McCallum *et al.*, 2008; El-taliawy *et al.*, 2017), ozonation (Ji *et al.*, 2015), chemical oxidation (Cheng *et al.*, 2016), membrane separation (Boukhelkhal *et al.*, 2016) have found to have efficient in water treatment in removing PhAcS. As these methods is laborious and costly, adsorption using biomass or waste from agriculture found to be highly advantageous (Kumar *et al.*, 2020).

As per the literature search, (Avinash *et al.*, 2019; Kumar *et al.*, 2019) used bi-products from the edible oil industry like groundnut seed cake powder (GNSCP), sesame seed cake powder (SSCP) and coconut cake powder(CCP) for the removal of Cr(VI), Co(II), Mn(II) and Cu(II). To the best of the knowledge of the authors, the same has not been used so far in the removal of PhAcS. In the present study, the authors have chosen Pregabalin, a neuropathic drug for the adsorptive removal using GNSCP and CCP. Pregabalin is a neuro-transmitter with the chemical formula C8H17NO2. Its water solubility is 11.3 mg/L. It has pKa1: 4.23 $\pm$ 0.10, Most Acidic; Temp: 25°C; pKa2:11.31 $\pm$ 0.10, Most Basic; Temp: 25° C. In light of its adverse effects, the present study has been carried out. The drug information is tabulated in Table 1.

MATERIALS AND METHODS

Analytical grade reagents have been used throughout the experimentation. Double distilled water was used throughout the experiment. 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 the TESCAN VEGA3 LMU model instrument.

Preparation of adsorbents

Groundnut seed cake and coconut cake were obtained from the edible oil industry nearby. These edible oil seeds, when processed for oil production, these cakes are obtained as byproducts. As these materials are hard masses, using a laboratory ball mill, these were ground into powder. Using an appropriate mesh, these powders were sieved to get particles of homogenous size. Such powders were placed under sunlight to make the powders dry prior to carbonization. These powders were washed with distilled water to remove any suspended matter and then dried at room temperature to remove moisture. These samples were stored in airtight containers for further processes. Such powder is carbonized by placing it in a crucible and heated until the entire mass is completely carbonized. Carbonized powders are stored in airtight containers to avoid contamination.

Preparation of Pregabalin solution: The stock solution of Pregabalin was prepared by dissolving an adequate amount of the substance in distilled water (100 mgL-1) and standardized. A series of varying concentrated solutions were prepared from the stock solution.

Methodology

Batch adsorption has been adopted for the removal of the drug by considering a series of flasks containing varying amounts of the adsorbent with the adsorbate (Pregabalin solution of volume 500 mL). By the addition of 0.1N HCl or 0.1 N NaOH solution, the pH of the adsorbate-adsorbent mixture is maintained. This mixture is continuously and thoroughly agitated until equilibrium is attained. Afterwards, the adsorbent was separated from the suspension through Whatmann.1 filter paper. The residual concentration of the formulation was determined by HPLC using a UV detector at 254 nm. The per cent removal of the drug can be calculated using the formula

$$\%\ efficiency\ of\ adsorption\ = \{(C_i - C_f)/C_i\}\ \times 100$$

$$Adsorption\ capacity\ q\ =\ V_s(C_i - C_f)/w$$

V_s is the volume of solution in L; C_i is the initial concentration; C_f is the final concentration and w is the weight of the adsorbent.

RESULTS AND DISCUSSION

The entire experimentation, such as optimization of parameters, kinetics, isothermal and thermodynamics, has been carried out in triplicate for obtaining more accurate results. All the results obtained from the optimization of the process are presented in Table 2.

Characterization of adsorbents

The surface area of GNSCP and CCP were found (from the BET method) to be 488 and 491 m2 g-1, respectively. Higher surface area values of the two adsorbents confirm the ability of adsorption. SEM images have clearly shown that the chosen adsorbents have fine porosity with a particle size in the range of 3-7 μm (Figure 1 and Figure 2). The bulk chemical composition of the same was studied using XRD. X-ray diffraction studies were carried out for

Table 1: Pregabalin and its Properties

S. No.	Parameter	Details
1.	IUPAC name	3-isobutyl GABA, (S)-3-isobutyl-γ-aminobutyric acid
2.	Brand name	Lyrica
3.	Chemical formula	C8H17NO2
4.	Molar mass	159.2
5.	Solubility	Soluble in DMSO, ethanol
6.	Boiling point/ melting point	191 OC
7.	Density	1.01 g/ cm3
8.	Appearance	White crystalline powder

Table 2: Optimization parameters for the adsorption of Pregabalin

S.No.	Parameter	GNSCP	CCP
1.	pH	7	7
2.	The temperature in (degree Celsius)	30	30
3.	Adsorbent dosage (g)	0.2	0.6
4.	Initial metal concentration (mg/L)	10	10
5.	Contact time (min)	60	60
6.	Qmax (mg/g)	9.84	9.76

the adsorbent and from the results, it was found that the adsorbent chosen is completely amorphous in nature (Figure 3 and Figure 4).

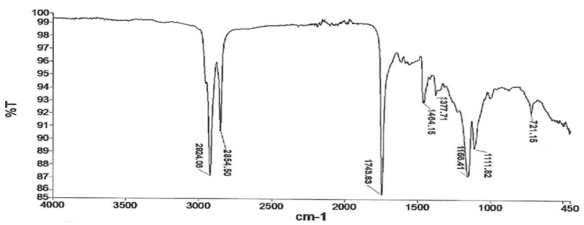

Figure 3: FTIR spectra of CCP

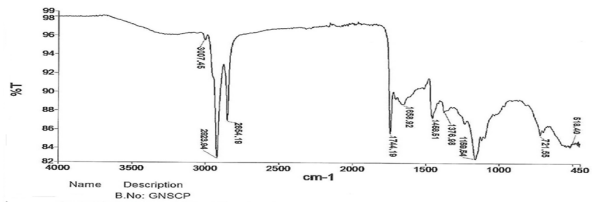

Figure 4: FTIR Spectra of GNSCP

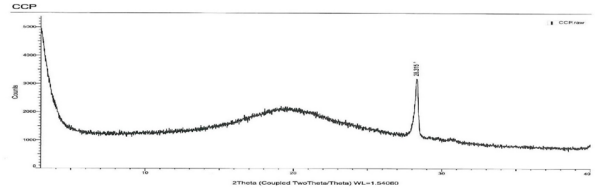

Figure 5: PXRD patterns of CCP

A sharp peak in the XRD spectrum of CCP infers the presence of silica in the adsorbent. The chemical structure of the surface and functional groups in the adsorbent are primarily influential for the adsorption capacity. Carboxyl groups, phenolic groups, hydroxyl groups, carbonyl groups and lactones groups are mostly responsible for surface activity. FTIR spectrum of the adsorbent confirms the presence of these functional groups in two selected adsorbents (Figure 5 and Figure 6).

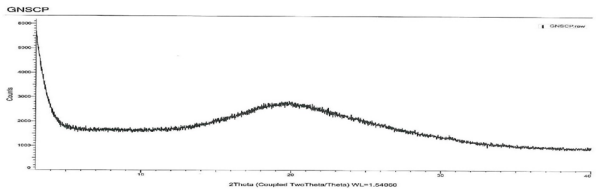

Figure 6: PXRD patterns ofGNSCP

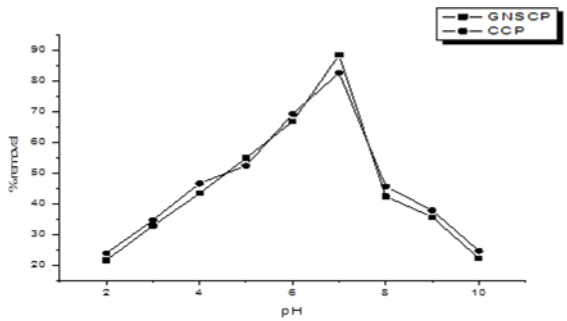

Figure 7: Effect of pH on the adsorption of Pregabalin

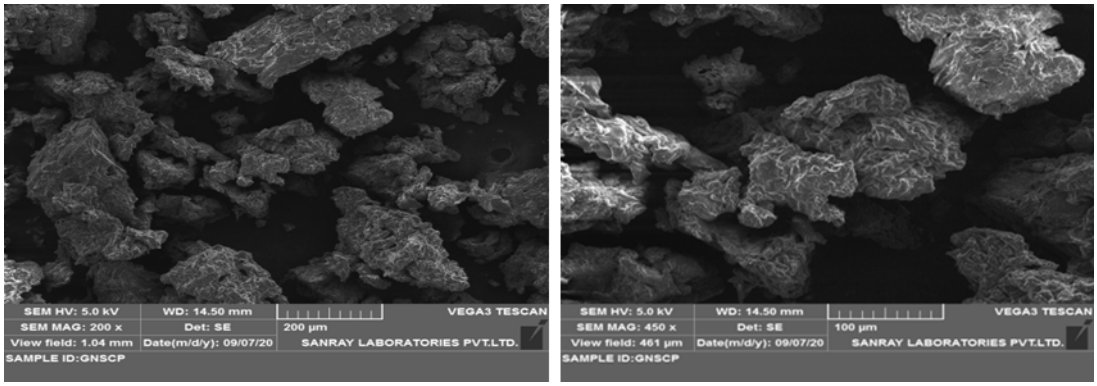

Figure 1: SEM images for GNSCP

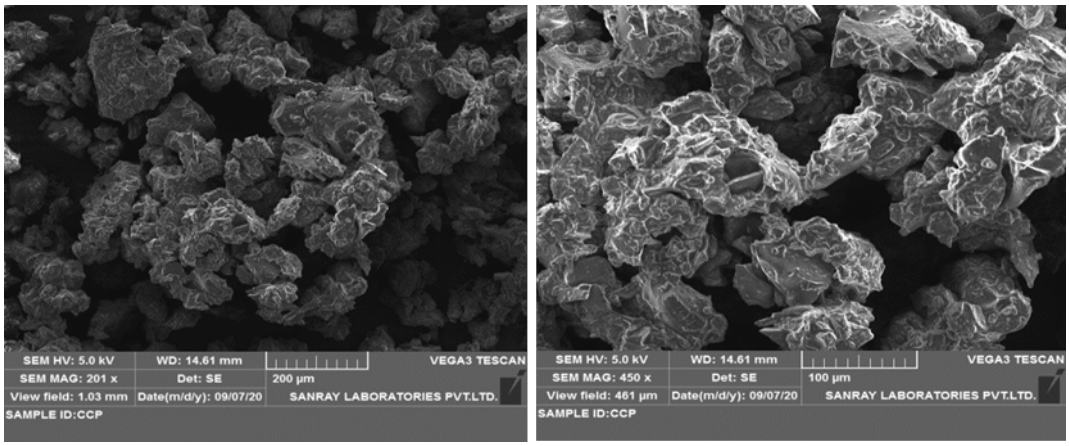

Figure 2: SEM images for CCP

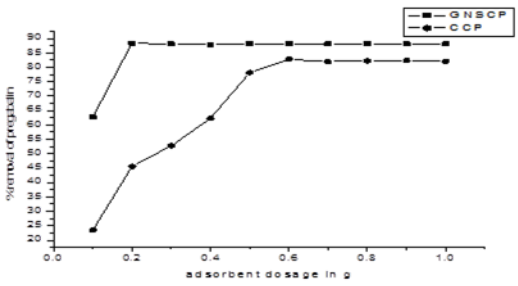

Figure 8: Effect of adsorbent dosage on the adsorption of Pregabalin

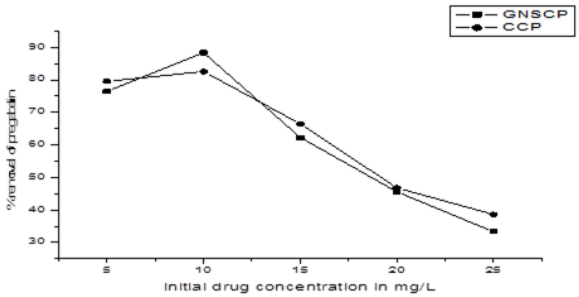

Figure 10: Effect of initial drug concentration on the adsorption of Pregabalin

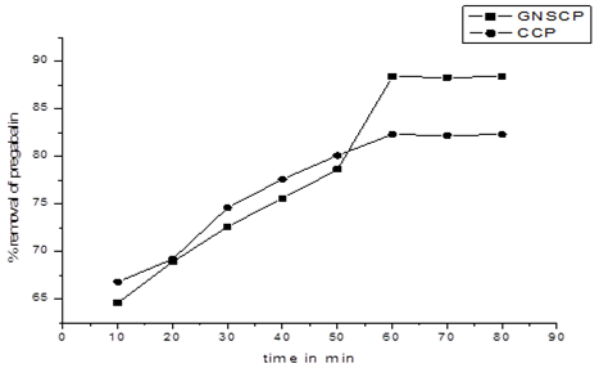

Figure 9: Effect of contact time on the removal of Pregabalin

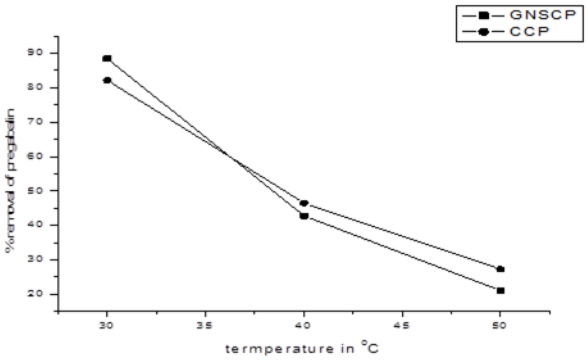

Figure 11: Effect of temperature on the adsorption of Pregabalin

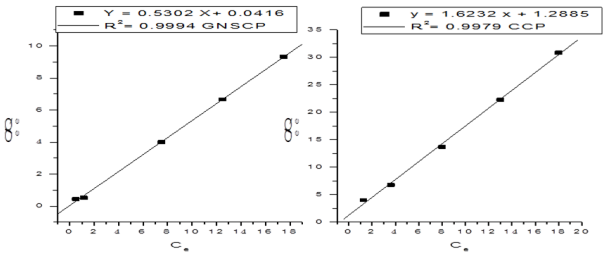

Figure 12: Langmuir adsorption isotherm for the adsorption of Pregabalin

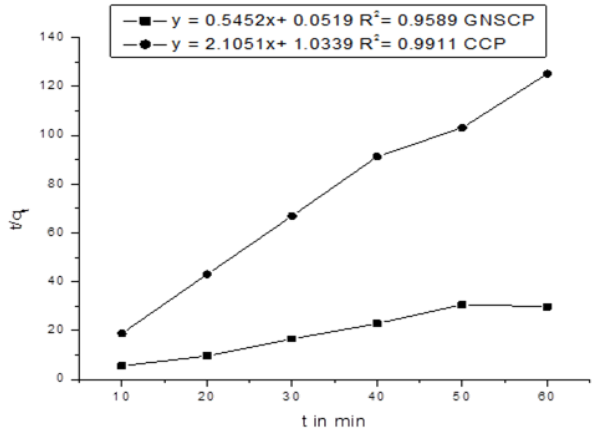

Figure 13: Pseudo second-order kinetic model for the adsorption of Pregabalin

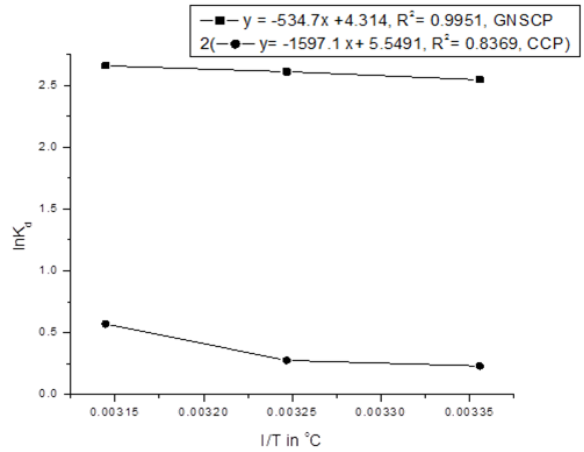

Figure 14: Effect of adsorbent dosage on the adsorption of Pregabalin

The effect of pH on the removal of Pregabalin using GNSCP and CCP is shown in Figure 7. From the results, it was found that the optimum pH for the adsorptive removal of Pregabalin is 7. Both the adsorbents showed similar results. Under strongly acidic conditions, the percent adsorption of the adsorbate is less. It gradually increases and reaches a maximum at pH 7. In the alkaline region (pH>8), the adsorption capacity of the adsorbate decreased. This may be attributed to the interaction between the adsorbate and the medium (either acidic or basic). Hence the adsorption of the drug is less in both acidic and basic conditions. 88.4% and 82.6% of the drug has been adsorbed by using GNSCP and CCP, respectively, at pH 7.

To ascertain the adsorbent dosage for the efficient removal of Pregabalin using GNSCP and CCP, a series of experiments have been carried out. By varying the adsorbent dosage from 0.1-1.0 g, the optimum adsorbent dosage for the efficient removal of the drug has been investigated. These results obtained are presented in Figure 8. These results showed that the removal of Pregabalin from aqueous solution was effective for 0.2 g for GNSCP and 0.6g for CCP per 500 mL of the drug solution. The same dosage has been fixed as the optimum adsorbent dosage. The effect of contact time on the adsorptive removal of Pregabalin is depicted in Figure 9.

By fixing the pH of the adsorbate-adsorbent mixture at 7, a series of experiments have been conducted to study the effect of contact time. Equilibrium time for the adsorption of the adsorbate is fixed from the experimental results. From the experimental results, the maximum adsorption has been found at 60 minutes. For both the adsorbents, 60 minutes is the optimum contact time. Remarkable changes have not been found beyond this time.

Figure 10 gives detailed information about the effect of initial drug concentration on the removal of Pregabalin using the two adsorbents. Experimentation has been carried out to fix the initial drug concentration by fixing adsorbent dosage (0.2 g GNSCP and 0.6g CCP), contact time (60 min) and pH (7.0). A series of Pregabalin solutions of concentration 10, 20, 30, 40, 50, 60, 70, 80, 90 mg L-1 were mixed in separate flasks with 0.2 g of GNSCP and 0.6 g of CCP. The resulting mixture has been agitated for 60 minutes. From the results, it was found that, as the concentration of the drug increases, due to lack of active sorption sites, the adsorption efficiency of the adsorbent decreased. At a concentration of 10 mg L-1, the maximum removal of Pregabalin using the adsorbents was found.

To establish the equilibrium temperature for the effective removal of Pregabalin using the adsorbents, a series of experiments were carried out. By fixing the adsorbent dosage (0.2 g of GNSCP; 0.6 g of CCP), contact time (60 min), pH (7.0) and initial drug concentration (10 mg/L), batch experiments were carried out at varying temperatures. From the results, the maximum adsorption of the drug was found at a temperature of 30o C. The results have been presented in Figure 11.

Adsorption isotherms

Among the many adsorption isotherms available, Langmuir, Freundlich and Temkin adsorption isotherms were used in the present study. 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 model can be represented as

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

Experimental results obtained from the isothermal analysis is presented in Table 3 These results showed that adsorption of the drug from an aqueous solution fit to Langmuir adsorption isotherm (Figure 12).

Various terms involved in the isotherm are qm and K is Langmuir constants related to the sorption capacity and sorption energy, respectively. Ce is the equilibrium concentration in mgL-1, and Qe is the amount of adsorbate adsorbed per unit weight of adsorbent. A plot of Ce / Qe against Ce was drawn, and the correlation coefficient from the graph was found to be 0.9994 with GNSCP and 0.9979 with CCP. This substantiates the fitness of the isotherm for the present study.

Qmax obtained for the removal of the formulation using GNSCP was found to be 1.88 mg/g and 0.61mg/g using CCP. Up to the knowledge of the authors, it was found that GNSCP and CCP have not been reported so far in literature for the removal of Pregabalin. Freundlich and Temkin's isotherms were also plotted and showed that with a relatively lower correlation coefficient, these two models are not suitable to explain the adsorption of the formulation on the two adsorbents.

Kinetic models of the present study

In explaining the mechanism of removal of the drug by the adsorbent, kinetic models are extremely helpful. Lagergren's pseudo-first-order kinetics and pseudo-second-order models are widely used among the many kinetic models developed Kumar *et al.* (2020); Avinash *et al.* (2019); Kumar *et al.* (2019).

The adsorption kinetics of pseudo-first-order was,

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

Where q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent, q is the amount of solute adsorbed at any time, and k is adsorption constant.

The pseudo-second-order kinetic model is described by the following equation,

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

Where q_t and q_e are the sorption quantity at time t and equilibrium, respectively, k is the rate constant. Thus a plot of t/ qt va t gives the pseudo-second-order adsorption. Pseudo-second-order rate constant was determined from the respective plots. The results were presented in Table 4.

It is inferred from the results that the sorption of Pregabalin using the chosen adsorbents followed pseudo-second-order kinetics. The same was presented in Figure 13. The correlation coefficient (R2) for the process was found greater than 0.9589 and 0.9979 indicating the fitness of the model for the present process. The constant rate value of pseudo-second-order reaction was found to be 0.88 and 1.326 min-1for GNSCP and CCP, respectively.

Thermodynamic studies

The practical application of any process is governed by thermodynamic parameters. The spontaneity of a process, both entropy and energy considerations must be taken into account in adsorption processes. To evaluate the thermodynamic parameters for the present adsorption system, the amount of Pregabalin adsorbed at equilibrium at different temperatures of 25, 35 and 45o C were examined. Using the following equation, thermodynamic parameters such as standard free energy change (ΔG), standard enthalpy change (ΔH) and standard entropy change (ΔS) were computed. The results obtained were presented in Table 5.

As the value of ΔH (6.7 and 3.1 Kcal /mol) obtained indicates that the adsorption of Pregabalin on GNSCP and CCP is an endothermic process and physisorptive by nature. The negative value of ΔG (-7.6 and -0.75 Kcal/mol) infers that the adsorption process is feasible and spontaneous in nature. The decrease in the degrees of freedom of the adsorbed species is a result of the negative value of ΔS (-8.2 cal/mol/K).

A plot between 1/T vs ln Kd is represented in Figure 14.

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

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

Table 3: Adsorption isotherm characteristics for the removal of Pregabalin using adsorbents

S. No.	Adsorber	Langmuir Adsorption isotherm			Freundlich Adsorption isotherm			Temkin adsorption isotherm		
		qmax	K	R2	KF	1/n	R2	B	A	R2
1.	GNSCP	1.88	12.74	0.9994	1.551	0.08	0.2838	0.117	1136	0.2802
2.	CCP	0.61	1.25	0.9979	0.33	0.25	0.79	0.099	1.007	0.8174

Table 4: Kinetic parameters for the adsorption of Pregabalin using the adsorbents

S.No.	Adsorbent	Pseudo-first-order kinetics			pseudo-second-order kinetics		
		qe	K1	R2	qe	K2	R2
1	GNSCP	1.75	2.36	0.5017	1.83	0.88	0.9589
2	CCP	0.44	-1.34	0.4717	0.475	1.326	0.9917

Table 5: Thermodynamic parameters for adsorption of Pregabalin using the adsorbents

S.No.	Thermodynamic parameter	GNSCP	CCP
1.	Standard enthalpy change (ΔH) in Kcal/mol	6.7	3.1
2.	Standard entropy change (ΔG) in Kcal/mol	-7.6	-0.75
3.	Standard Gibbs free energy (ΔS) in cal/ mol K	-27.9	-11.1

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

Applicability of the adsorbents to industrial effluents

Industrial effluent sample containing Pregabalin as a contaminant has been collected and retreated to remove color, suspended particles, if any. Such a sample of volume 500 mL is taken in two separate flasks and mixed with 0.2 g of GNSCP and 0.6 g of CCP. At a pH value of 7, the temperature of 27oC, the mixture is agitated for 60 min. After the Predetermined time, the mixture is filtered and the concentration of Pregabalin in the filtrate is found using the HPLC method. The percent removal of the drug from the industrial effluent was found to be 88 using the two adsorbents.

CONCLUSION

Adsorptive removal of Pregabalin using GNSCP and CCP has been optimized at a temperature of 30o C, pH of 7, contact time of 60 min, initial drug concentration of 10 mg/L and adsorbent dosage of 0.2 g (GNSCP) 0.6 g (CCP). With constant rate values of 0.88 and 1.326 g/mg/min, the adsorption of the drug fits for the pseudo-second-order kinetic model. Using both adsorbents, the adsorption of Pregabalin fits Langmuir type adsorption isotherm. A negative value of ΔG indicated that the adsorption of Pregabalin on GNSCP and CCP is spontaneous and feasible. With the optimized parameters, the adsorbents have been tested for industrial effluent and found to have removed 96 % and 89.3 % of the drug-using GNSCP and CCP, respectively.

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Conflict of Interest

The authors declare that there are no conflict of interest for this study.

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