



Original article

Waste shrimp shell mediated Chitosan-Magnesium Oxide nanocomposite: Synthesis, characterization and exploitation towards acenaphthene removal from aqueous solution

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ABSTRACT

Keeping the sustainability concept in view, a green, biocompatible, eco-friendly, and advantageous nanocomposite was fabricated by impregnation of chitosan derived from waste shrimp shells onto Magnesium oxide nanoparticle (MgO) for exploiting in acenaphthene (ACN) removal from wastewater resources. The tested nanocomposite showed a high potential for ACN adsorption at pH 5.5. The thermodynamic evaluations laid the spontaneity nature of the process ($\Delta G \leq -25.93 \text{ kJmol}^{-1}$) bearing a ΔH value of $12.701 \text{ kJmol}^{-1}$ which shows a favorable physisorption phenomenon. Kinetic evaluations demonstrated that the studied adsorption system conforms to pseudo-first order model to a greater extent. Other kinetic evaluations (Dumwald-Wagne/ Boyd model) revealed the important role of film diffusion in such an adsorption system, especially in the initial stages of the process. The equilibrium scrutinization under isothermal conditions displayed that the process has proceeded via mono-layer adsorption with a q_{max} value of 116.88 mg/g (at 298 K), for which Langmuir model showed a high goodness-of-fit. Overall, the new green adsorbent was highly advantageous in removal of ACN, and hence it is worth to be checked for the possibility of removing similar contaminants from polluted agricultural wastewater resources.

1. Introduction

Contamination of water resources is a universal issue, owing to industrial, municipal, and agricultural activities. In an emergency to overcome the water scarcity issue, there is a demand to apply efficient and sustainable methods to reach enhanced water supply levels beyond the traditional routes [5,6]. Drastic industrial and urban expansion have raised enormous anthropogenic activities which, beside the natural sources, cause emission of pollutants, like poly-aromatic hydrocarbons (PAHs), into the environment [45]. PAHs released into environment

spring from natural resources, like forest fire, volcanic eruption, and brush fire, as well as from man-made activities, like oil spilling, partial combustion of fuels, other industrial spillages, which are of huge concern at present around the universe [1]. The extraneous characteristics of PAHs comprise heterocyclic ring arrangements, thermo-stability and hydrophobicity which rendered them recalcitrant and super persistent in the ecosystem [48]. They are much toxic, carcinogenic, mutagenic and immune-toxicogenic to several life types. PAHs tend to exist in aquatic sources as a result of i) fossil fuel-incomplete combustion, ii) exploitation/utilization of petroleum and iii) biogenic sources in

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nature. They transfer into water resources through direct deposition or simultaneous discharge of oil/fuel products [19]. Hence, it is mandatory to decrement the risk associated to PAHs persistence in water sources by incorporating effective methods in water treatment methodologies.

Acenaphthene (ACN) is identified to be an organic compound affiliated to the class of poly-aromatic constituents [34]. ACN possesses comparatively lower range of solubility (2×10^{-4} mg/L) and greater half-life period compared to phenanthrene (6.8×10^{-4} mg/L) [53]. Various reports can be found in literatures with focus on PAHs toxic impacts to aquatic creatures and bioaccumulation property along the food chain [10,21,4]. The maximum permissible limit for acenaphthene concentration by international associations is 0.1 µg/L in surface waters. ACN and its metabolite compound, anthraquinone, are much noxious to human beings, because of their photosensitizing impact. Indeed, due to the omnipresence and toxicity effects of ACN and its derivatives, its complete sequestration is the need of hour. It can be potentially decontaminated using several technological mechanisms such as electrochemical, ion exchange, solvent extraction, chemical oxidation, reduction, adsorption, precipitation and even filtration [70]. Perhaps, several bio-systems (*Escherichia coli*/*Bacillus*) have been utilised generally to sequester these ACN components from contaminated sources [68]. Owing to the excess time consumption and associated expenses, biological/chemical means of degradation has been substituted by adsorptive mechanisms [46,60], with escalating usage of nanocomposites [31].

Adsorption technique has been elucidated as the most economical and simplest process for PAHs sequestration, as well as for pesticides, pharmaceuticals and endocrine disrupting compounds, and heavy metals, owing to its versatility, less cost, ease of process, and maximum efficiency [15,33]. Several adsorbent materials have been utilised for organic micro pollutant removal which include commonly employed activated carbon, carbon nanotubes, biomass waste materials [32], clays, mesoporous silica, and resin matrices [16,66]. Every adsorbent possesses unique features that enable them to decontaminate several classes of pollutants. Scrutinizing literature shows a broad usage of transition metals oxides as nano-sorbents [18,54], owing to their high surface/volume ratio, low cost, convenient production and availability, and nontoxic nature. On the other side, nanosized components, including metal nano-oxides, have found an important part in amelioration of other adsorbents and producing novel composites [31,38]. In the recent years, besides transition metals, nano-oxides of other metals have also been exploited for modification of adsorbents and fabrication of useful composites, both for catalytic and adsorptive usages [18,64]. In this context, among others, many metal oxide nanoparticle-modified polymers have been exploited as adsorbent for different contaminations [25,69].

Chitosan, (CS), a natural polymeric compound, is produced by commercial means through the chitin hydrolysis in presence of alkali medium. In spite of being advantageous in many areas, its biocompatibility, renewability and biodegradability, its usage is much restricted in unmodified form. It can also aid in water/waste effluent purification, and heavy metal components elimination from aquatic sources [7]. It exhibits unique pattern of chemical visualization, structure inculcating hydroxyl/amino groups, and a great pollutant uptake efficacy [8,9]. The major demerit of its usage in adsorption technology is the narrow basic features along with excessive swelling characteristics and gel development which make its separation as well as its recovery very tedious. To overcome such drawbacks, MgO-ameliorated chitosan nanocomposite can be effectively serves as an adsorbent, which is in fact a three-dimensional cross-linking polymeric matrix impregnated with magnesium nano-oxide. Similar studies have shown that MgO-modified polymers can serve as valuable adsorbents [26,28], due to their large surface area, high mechanical stability, high adsorption capacity, etc. In fact, the MgO-impregnated chitosan possesses a large surface area, which was exploited for adsorption of acenaphthene from aqueous media as well industrial waste outlets which would forgo contamination

issues. The MgO/chitosan nanocomposite was characterized by various techniques and, as an economic material, was tested to scrutinize its adsorption properties for the ACN adsorption. In addition to characterization studies, vast experimental analyses were performed to optimize the adsorption process, along with extensive kinetic, isothermal and thermodynamic evaluations of the adsorption system.

2. Methodology

2.1. Materials

Analytical grade of NaOH, $\text{Mg}(\text{NO}_3)_2$, HCl, Sodium tri-polyphosphate, acetonitrile and acenaphthene (HPLC grade), with purities >99 %, were received from Merck, Germany. Chitosan and liquid NH_3 were supplied from Uma Scientific suppliers, Chennai, Tamilnadu. Shrimp shells were gathered from local seashore markets. Deionized water was utilized throughout all experimental analyses.

2.2. Preparation of MgO nanoparticle

The co-precipitation procedure was exploited for fabrication of MgO nanoparticles. To find optimal circumstances for fabrication of MgO nano-particles, utilizing magnesium nitrate, different conditions were tested. For the purpose of final MgO nanoparticles, 1.48 g $\text{Mg}(\text{NO}_3)_2$ was taken and dissolved in 100 mL of distilled water. Then, using magnetic stirrer, the mixture was agitated for 24 hours at 60°C. Afterward, 0.1 M NaOH solution was added in drop wise manner and stirred again for 3.0 hours. After this period, the whole mixture was refluxed at 100°C for 12.0 hours and, then, the acquired substance was isolated by centrifugation and oven-dried after removing the impurities by rinsing. The final magnesium oxide powder subjected to calcination at 600°C, using a furnace, and magnesium oxide nanoparticles were acquired in the form of white powder which was stored to be used for amelioration of chitosan.

2.3. Chitosan fabrication

Shrimp shells in frozen circumstance were firstly thawed at ambient temperature and organic and other type impurities were removed by rinsing with tap water. Then, they were boiled at 100°C for 30 minutes to removes the tissues, and were dried at 85°C for 100 minutes. The shell powder was attained by crushing, blending and grinding the dried shell. Demineralising of the obtained powder was performed by utilizing 2 M HCl at 65°C for 160 minutes, by stirring with a magnet stirrer. Then, the powdered shells were deproteinized using 3.0 M solution of NaOH at 80°C, for 120 min. Traces of pigments were omitted by heating at 200°C, and after several times of washing, the material was dried for 7 hours at ambient temperature. Underneath vacuum and constant agitation, using NaOH at 110°C, the obtained chitin was deacetylated in a 6-hour duration [44]. Then, it was cooled at room temperature, for 30 min. At the final stage, chitosan was rinsed with distilled water till the filtrates reach pH 7 and dried at 60°C for a 24-hour period.

2.4. Preparation of nano-chitosan using ionic gelation method

1.5 g (w/v) of chitosan suspended in 100 mL of distilled water, then dissolved by adding 0.5 mL acetic acid and the solution was stirred for 25 minutes. After that, 1.83 g of sodium tri-polyphosphate (STPP) was poured into 100 mL distilled water and, then, this solution was poured drop by drop into chitosan solution and stirred for 40 minutes to get a white colour precipitate. Chitosan nanoparticles, as a milky white emulsion, were fabricated betwixt STPP and chitosan solutions owing to ionic cross linking. Afterward, final solution was kept overnight so that nano chitosan got settled at the bottom. The solution was decanted and then the thick suspension of settled nano chitosan was preserved in the refrigerator.

2.5. Synthesis of chitosan/MgO nanohybrid

Chitosan/MgO (CS/MgO) nanocomposite was fabricated utilizing a one pot solution casting procedure. Briefly, 2 gm of chitosan powder (medium molecular weight; 85 % DDA) was dissolved in 100 mL of aqueous acetic acid solution (2 %; v/v) underneath agitation for 12 hours at ambient temperature. Then, 2 gm of nano magnesium oxide was poured into this solution and mixed by re-stirring for 12 hours until a clear solution was acquired. The obtained viscous solution was casted in a Petri dish and dried over a night at ambient temperature (25 °C). Neutralization and phase separation was done by immersing the Petri dish into NaOH solution (0.1 M) [42]. The fabricated solid films were oven-dried for 6 hours at 80°C. Then, the solid films were washed with several times for the aid of purification and again were oven-dried for 2 hours at 65°C. For comparative studies, a film of pure chitosan, bereft of MgO nanoparticles, was fabricated using the similar method.

2.6. Characterization analysis

Chitosan/MgO nanocomposite powder structural characterizations was conducted by XRD (X-ray diffraction instrument), FTIR (Fourier transform spectroscopy) as well as SEM (scanning electron microscopy) techniques. The structural pattern of such nanocomposite was estimated exploiting XRD analyser with Cu K α intensity (wavelength of about 1.5412 Å) radiation source, recorded from various angles of 2 θ ranging betwixt 20–80. [47] Surface topology, size and morphology of fabricated chitosan nanocomposite material was evaluated via SEM analyses. The FTIR intensity interpreting (6400 FTIR, Thermo scientific nicholet, Washington, USA) was exploited to determine the involved functional moieties existing in the fabricated nanocomposite.

2.7. Adsorptive application of chitosan/MgO nanocomposite towards ACN removal

The adsorptive analysis was estimated using batch experiments for varying quantities of acenaphthene levels from 5 to 80 mg/L, applying chitosan/MgO nanocomposite as a utilized adsorbent (2.0–80.0 mg). The impact of temperature was appraised betwixt 25–45 °C along with reaction time from 2.0 – 70.0 minutes and pH impact betwixt 2.0–10.0. The acenaphthene samples (100 mL) with varying concentrations carefully poured into 250-mL Erlenmeyer containers were submitted to rapid stirring at a monotonous rotating velocity of 400 rpm in a revolving temperature-set shaker. 0.1 M HCl/NaOH solutions were exploited for pH adjustments of aqueous phases. At the specified time, by the aid of a UV-Visible 1600 instrument (Shimadzu, Japan), the remaining acenaphthene concentration in the tested solutions were measured by UV-Visible spectrophotometric method. To maintain data accuracy as well as the precision, the adsorption analyses in each elected set of conditions were employed in triplicates and the averaged outcomes were exploited. The influence of acenaphthene quantity (5–80 mg/L), contact time (10–50 min), pH level (2–10), dose of composite (20.0–80.0 mg), and temperature (25–45°C) was attentively scrutinized, along with estimating the equilibrium, kinetics, thermodynamics properties. The percentage of acenaphthene sorbed from aqueous media was determined by the mathematical relation of acenaphthene adsorbed (%) = $(C_i - C_f) \times 100 / C_i$, where C_i and C_f denote the acenaphthene concentrations at the starting (initial) point and after the specified contact time (mg/L).

2.8. Equilibrium and thermodynamic studies

The adsorption capacity is dependent on the adsorbent affinity for the solute, and the adsorption isotherms are useful curves that may quantitatively characterize the adsorbate distribution between the liquid and solid phases at a constant temperature [49]. For precise investigation of the nature and mechanism of ACN adsorption from

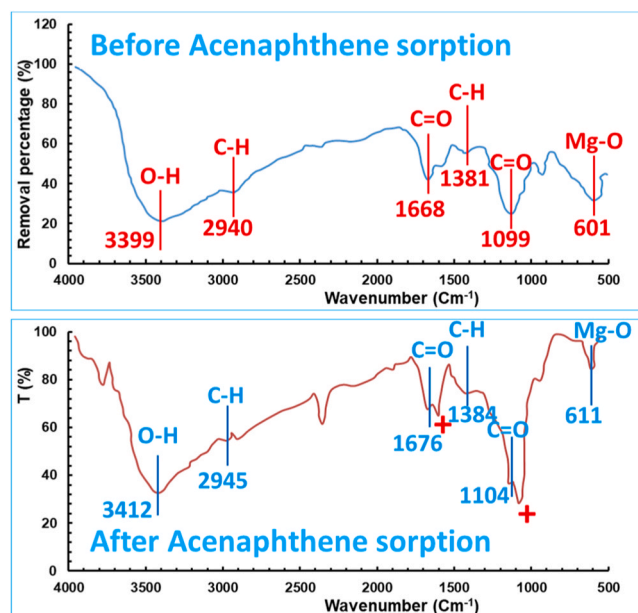


Fig. 1. FTIR spectra of chitosan/MgO nanocomposite before and after Acenaphthene sorption.

aqueous solutions onto the surface of chitosan/MgO nanocomposite, isothermal evaluations of the adsorption processes are highly helpful. These evaluations were carried out batchwise at 298 K, utilizing 0.05 g of the chitosan/MgO nanocomposite, 100-mL portions of solutions (pH 5.5) with different ACN concentrations ranging from 5 to 80 mg/L, and a contact duration of 60 min. For thermodynamic calculations, the equilibrium data were performed at three other temperatures (288, 308 and 318 K). Eight adsorption isotherms were used in this investigation, four of which had two parameters and four of which had three.

2.9. Kinetic considerations

Understanding the kinetics of adsorption processes and determining the ideal conditions for developing large-scale adsorption systems need careful examination of adsorption rate data [49]. By fitting experimental adsorption rate data with model equations, kinetics assists researchers in determining the rate-controlling step [23]. In order to improve operating conditions for the batch adsorption process, the kinetics of adsorption were therefore investigated using a variety of theoretical models, including pseudo-first and pseudo second order models, along with Dumwald–Wagne and Boyd models. The nonlinear form of equations was utilized in each of these models to determine which kinetic model best suited the adsorption processes. For this purpose, batchwise experiments were performed at 298 K, utilizing 0.05 g of the chitosan/MgO nanocomposite, 100-mL portions of solutions (pH 5.5) with different ACN concentrations (i.e., 15, 30, and 60 mg/L), and a varying contact durations ranging from 0 to 40 min.

3. Results and discussions

3.1. Characterization interpretation of CS/MgO nanocomposite

Structural constituents of CS/MgO composite adsorbent were identified exploiting FTIR, SEM, XRD and EDS analysis. Fig.1 shows FTIR spectra of composite adsorbent prior and after sorption of Acenaphthene. Major functional groups of CS emerged at about 3400 cm⁻¹ (O-H group), 2940 cm⁻¹ (C-H bond; CH₃ moieties), 1670 cm⁻¹ (amide carbonyl moieties), 1380 cm⁻¹ (CH₂ moieties bending vibration) and 1100 cm⁻¹ (asymmetric C=O vibration) [27]. After adsorption process, although some bonds of chitosan in CS/MgO composite have shifted to

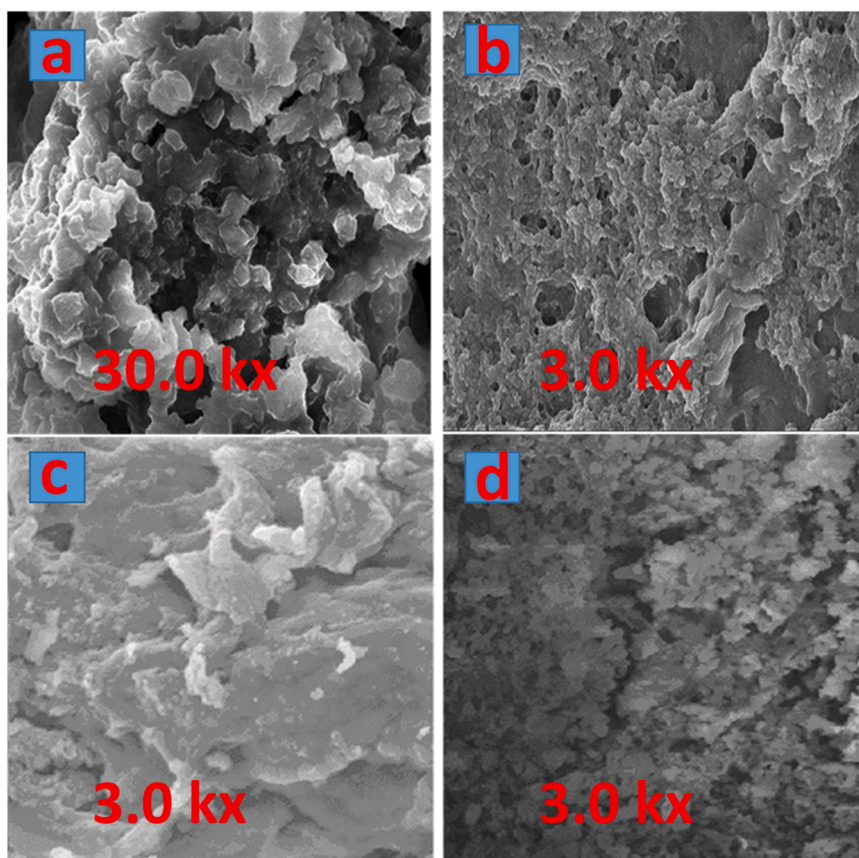


Fig. 2. SEM images of (a) MgO, (b) CS, (c) CS/MgO prior to sorption, and (d) CS/MgO after sorption process.

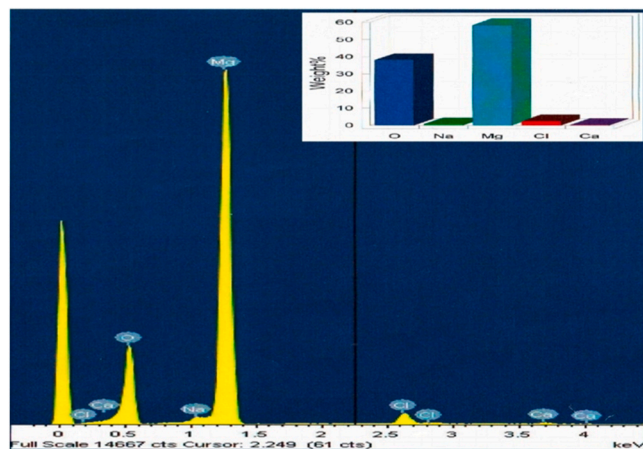


Fig. 3. The result of EDX analysis of nanocomposite.

more energetic wavenumbers [13], the presence of characteristic band of MgO at about 600 cm^{-1} is obvious in both spectra [12,56]. After adsorption, the prominent C-H bonds and C-C bonds established that ACN has been strongly up-taken onto CS/MgO composite. The related FTIR peaks can be observed in the ACN-loaded composite (Fig. 1), specially at 1080 and 1600 cm^{-1} [63].

FESEM technique was exploited to evaluate the morphological characteristics and surface distribution of MgO nanoparticle component (Fig. 2a) embedded onto the chitosan polymeric matrix. The micrographs of chitosan (Fig. 2b) were compared with micrograph images of MgO (10 %) incorporated with polymeric array (Figs. 2c and 2d). Fig. 2a with a high magnification (30,000) reveals the nanostructure of the MgO

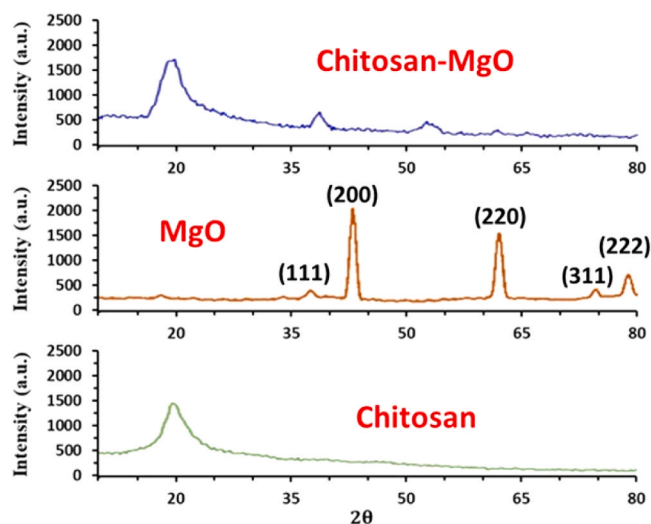


Fig. 4. XRD Analysis of MgO, CS and CS/MgO.

particles, having a size range of 5–12 nm approximately. However, unfortunately, because of the low thermal stability of chitosan and chitosan/MgO composite, taking their FESEM micrographs with high resolution is not possible. The composite which contain 10 wt% MgO exhibited some spots on the polymeric array, both before and after Acenaphthene adsorption, which were distributed in homogeneous pattern (Figs. 2c and 2d).

Also, EDX findings (Fig. 3) for the chitosan/MgO nanocomposite vouchsafed the inclusion of MgO in the structure of the polymeric array (Riyadh et al., 2018).

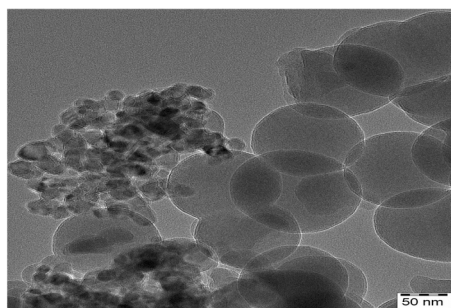


Fig. 5. TEM depict of CS/MgO nanocomposite.

Table 1

BET parameters of studied components.

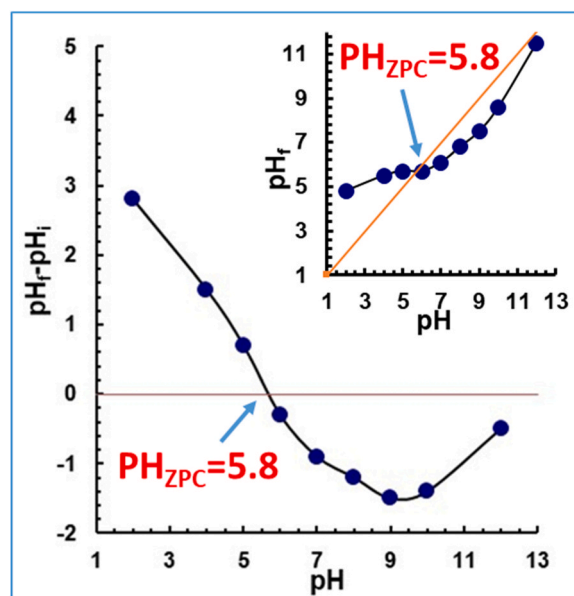
Component	BET Coverage (m ² /g)	Pore volume (cm ³ /g)	Mean Pore width (nm)
MgO	8.682	0.0284	10.02
Chitosan	1.432	0.0099	18.29
Chitosan/MgO composite	2.126	0.0064	10.29

The structural phase constituents of CS/MgO composite adsorbent were estimated using XRD interpretation. Fig. 4 elaborates the distinguished XRD peaks of CS/MgO composite adsorbent, compare to those of pristine chitosan and MgO nanoparticles. It was revealed that the XRD pattern of chitosan showed a peak at 2θ of 20.22° , emphasizing amorphous morphology. The peaks observed at 37.12° , 43.21° , 62.54° , 74.93° and 78.91° in the XRD pattern of pure MgO were respectively related to (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2), which are characteristic peaks of cubic MgO nanoparticles with standard JCPDS card number 04–0829 [52]. The XRD pattern of the composite exhibits the existence of MgO nanoparticles by the peaks at 2θ of 37.21° , 56.11° , and 62.01° (Fig. 4). With the addition of MgO, the major peak of chitosan ($2\theta \approx 20^\circ$) remained unchanged in the composite, indicating that the crystallinity of chitosan was not altered by MgO particles. Therefore, it may be hypothesized that MgO did not nucleate chitosan and that MgO nanoparticles had a little effect on the crystallinity of chitosan [62].

The TEM micrograph (Fig. 5) at lower magnification exaggerates that proper free-standing and large pellet-like pattern of chitosan/MgO composite. An enlargement over the depict states that these pelletized patterns are transparent, semi-circular with a definitely identified outline which dominated the synthesis of such nanocomposite. Furthermore, the dark segments in these images prioritized that edges of such composite are regular.

BET isotherms of chitosan, MgO particles, chitosan/MgO composite are represented in Table 1. All three are expressing type IV isothermal curves. Perhaps the very narrower loops of hysteresis at higher (chitosan/MgO nanocomposite) and moderately relative pressure (MgO nanoparticles) portray the existence of mesoporous structure [11]. The resemblance among chitosan and chitosan/MgO expresses the likely porous patterns of these 2 components (Table 1). BET surface estimations of MgO, chitosan and chitosan/MgO composite are 8.682, 1.432 and 2.126 m²/g. The mean pore distribution of the nanocomposite is 10.29 nm.

Chitosan was also exposed to temperature to assess the structural variations during heating, and thermal features of chitosan/MgO and pure chitosan were compared. In this analyses, the data showed that MgO addition can enhance the thermal stability of chitosan. Based on TG analyses outcomes, the initial mass reduction at 40–60°C could be accounted to absorbed moisture removal. The next mass reduction at 280–330°C could be confined to the thermal breakage of amino and hydroxyl methyl groups of chitosan. The degradation level due to heating approached 36.62 % for 0.5 % MgO (at 380°C) and 86.24 % for

Fig. 6. pH_{ZPC} curve of CS/MgO nanocomposite.

1 % MgO (at 550°C), with temperatures higher than those needed for chitosan in pure form (280°C). This incident highlights that MgO particle binding efficiently delineates the chitosan from weight loss and also hinders more effectively with the incrementing quanta of particles. Compared with purer chitosan, composite can sustain its integrity at elevated heating levels. Hence, MgO dispersion can have a barrier impact for chitosan thermal degradation and thereby delaying the mass loss of chitosan effectively.

The zero point of charge is a common way to describe the electrical state of an adsorbent surface in aqueous phases (ZPC). This point can be defined as the solution's condition where the surface charge density is equal to zero. The pH of point of zero charge (pH_{ZPC}) of CS/MgO nanocomposite was examined using pH drift protocol and NaCl as electrolyte [58] in which pH_{ZPC} of this CS/MgO was evaluated to be 5.8 (Fig. 6). At pH lower than pH_{ZPC}, the CS/MgO composite surface contains positive charges and at pH greater than pH_{ZPC} it contains negative charges.

3.2. Effects of physiochemical factors

The impact of acenaphthene solution pH, using CS/MgO nanocomposite, was evaluated at pHs ranging from 2 to 10, using composite dose of 50 mg and aqueous phase volume of 100 mL with ACN concentration of 20 mg/L. The adsorptive outcomes of acenaphthene onto such nanocomposite were pH influenced. The outcomes in Fig. 7a depicts that the acenaphthene percentage sorption changed with a changing pH from 2.0 to 10.0. The percentage of acenaphthene adsorption onto CS/MgO composite altered from 25.35 % to 93.95 % and reached the maximum at pH 5.5. Such an observation might be owing to dominant electrostatic interactions existed among the positively charged composite sites (pH_{ZPC}=5.8) and the electron-rich acenaphthene molecules, as implied by other workers [17]. The effect of pH increment caused a big decrement in acenaphthene removal percentage at high pHs, so that further increase of basic strength of the aqueous solutions gave way to the decrease of removal of acenaphthene molecules to 32.83 % (at pH 10.0). At higher pH ranges, in addition to lower solubility of ACN [31], hydroxyl ions undergo competition with hydrocarbon compound for occupying adsorptive sites on the composite surface and, hence, rendered to reduced acenaphthene removal. Such indications suggested that the best pH (optimum) for acenaphthene sorption is 5.5.

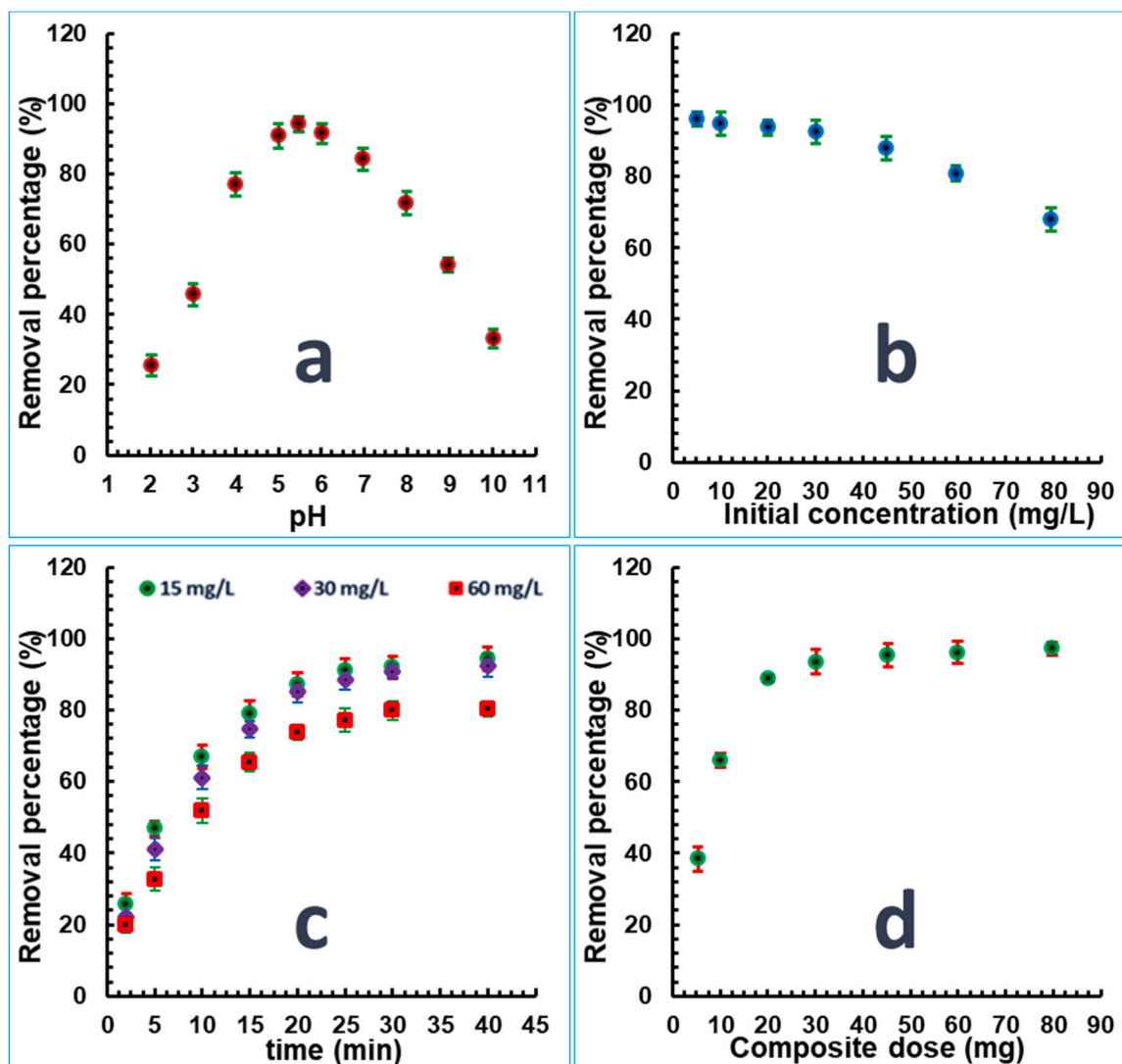


Fig. 7. Effects of pH (a), initial concentration (b), contact duration (c), and composite dose (d). Conditions utilized in studding of each factor have been mentioned in the text.

The initial concentration of acenaphthene hydrocarbon is a parameter that studding its impact is noteworthy (Kumar et al., 2019). In this research, the profound impact of several initial acenaphthene concentrations onto CS/MgO composite was displayed by studding various concentrations ranging from 5.0 to 80.0 mg/L, using composite dose of 50 mg and aqueous phase volume of 100 mL with pH adjusted at 5.5. The outcomes were represented in Fig. 7b. When the sample concentration of acenaphthene was enhanced from 5.0 to 80.0 mg/L, the removed hydrocarbon percentage drastically reduced from 96.01 % to 67.13 %. Anyhow, various ranges of concentration were recruited for studding the sorption properties of the composite.

The contact duration between hydrocarbon adsorbate and composite adsorbent is yet another key parameter that possess a significant role in acenaphthene sorption phenomena. The impact of contact duration on the adsorptive efficacy of CS/MgO composite in sorbing acenaphthene compound was evaluated by fixing all other involved parameters as constant (initial sample concentration of acenaphthene: 15.0, 30.0, 60.0 mg/L, recruited dose 50 mg, and weakly acidic pH (5.5)). Fig. 7c exhibits that the removed acenaphthene percentage increased slowly from 25.37 % to 93.97 % at 15.0 mg/L, 22.60–92.33 % at 30.0 mg/L, and 19.47–80.18 % at 60.0 mg/L, owing to the increment in contact duration from 5.0 to 40.0 minutes. Further addition of time duration up to 50 minutes did not cause a substantial increment in hydrocarbon

removal and the changes were marginal. Practically speaking, longer contact duration may require maximum investment and increased operating expenses for real time applications. Hence, the optimum contact duration for acenaphthene sorption onto CS/MgO nanocomposite is lower than 50 minutes. Such contact time for acenaphthene removal is too shorter when compared with that of other sorbent materials listed in previous literatures [31].

Adsorbent dose is a key parameter that has to be promptly monitored during adsorption phenomena. The impact of adsorbent quantity on acenaphthene adsorption was determined by altering the dose range of CS/MgO nanocomposite from 5.0 to 80.0 mg by fixing all other impacting parameters as constant, i.e., pH 5.5, contact time 50 minutes, initial acenaphthene concentration 50 mg/L, and atmospheric temperature. Fig. 7d depicts that the removed acenaphthene percentage increased from 38.35 % to 96.91 % as the composite dose varied from 5.0 and 80.0 mg, respectively. Such an increase in the removal percentage is ascribed to the enhanced composite surface distribution and maximum accessibility of adsorptive sites as composite sorbent is increased [24]. Anyhow, further increment in composite dose up to 150 mg possessed minimal impacts on acenaphthene removal. Henceforth, the optimum economical composite dose of CS/MgO for Acenaphthene removal in the above-mentioned conditions is 50 mg. All the experimental runs were done thrice and error rate was 3 % only, along

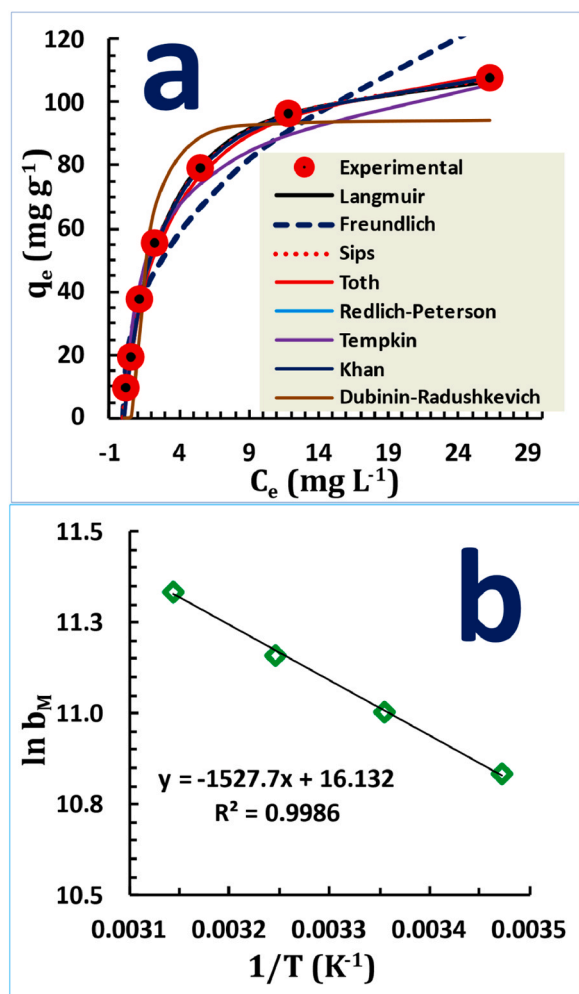


Fig. 8. Fitness of equilibrium data with different isotherm equations (a) and fitness of thermodynamic data with vant Hoff equation (b).

with standard deviation of 0.05.

3.3. Isotherms of adsorption

Sorption isotherms represent the equilibrium relationships between sorbate level in solution phase and on sorbent phase at definite conditions. The isothermal studies have fundamental importance in optimization of system designs for adsorption processes. Several isotherms have been introduced as mathematical expression for describing equilibrium relationship between adsorbates and adsorbents. In the present work, the outcomes of sorption tests of ACN at various levels spanning from 5.0 to 80.0 mg/L on a constant dose of composite were appraised for completing isothermal studies at different temperatures. For this goal, the q_e values of chitosan/MgO for ACN removal at optimum pH (5.5) as a function of equilibrium ACN concentration (C_e) were plotted and fitted to Toth, Redlich-Peterson, Khan, Sips, Dubinin-Radushkevich, Tempkin, Langmuir, and Freundlich isotherms to model sorption outcomes. Fig. 8a visually displays the fitness of data with the utilized two- and three-parameter adsorption isotherms [3,43]. Additionally, isothermal parameters and some statistical indices have been computed and listed in Table 2. From the reported outcomes in Table 2, it can be grasped that Langmuir isotherm equation has a great R^2 (0.9996) and low χ^2 (0.287) Δq (5.808 %) values which are sufficient to prove that a mono-layer adsorption has happened. Also, it should be noted the neither R^2 values nor the statistical indices of three-parameter models have a stark difference with the corresponding values in the Langmuir

model. On the other hands the values of n in all the three-parameter models are near unity. Such outcomes lay the reality bare and show that the adsorption is definitely mono-layer and the Langmuir model is capable of elucidation of the sorption process, since such circumstances cause the three-parameter models to be transformed to the Langmuir model [3,49]. Such outcomes vouchsafe that the adsorption process is progressed homogeneously via mono-layer deposition of ACN molecules on the sorption sites of the synthesized chitosan/MgO [22,49]. Some other results also can be drawn from the isothermal assessments. For instance, the E value obtained from the Dubinin-Radushkevich model (0.197 kJmol⁻¹) is low which shows that the process is of a physisorption nature [2].

3.4. Thermodynamic considerations

The thermodynamic aspects of ACN sorption on chitosan/MgO nanocomposite were scrutinized by computing Gibbs free energy change ΔG (kJmol⁻¹), enthalpy change ΔH (kJmol⁻¹), and entropy change ΔS (Jmol⁻¹K⁻¹). A correct thermodynamic equilibrium constant should be dimensionless and independent of adsorbate concentration. Therefore, constants like K_d and K_c are not suitable for thermodynamic calculations, as they have a dimension and are both dependent on the adsorbate concentration ([36,39]; Lima et. al, 2019). For calculation of such parameters, one should evaluate the effect of temperature on the process by performing equilibrium studies at different temperature and obtaining a dimensionless equilibrium constant [35,51,59]. For any sorption system, the Gibbs free energy change can be computed by equation $\Delta G = -RT \ln K_e$ where K_e is the thermodynamic dimensionless constant, R is the gases constant (8.314 Jmol⁻¹K⁻¹), and T is temperature in K. The value the thermodynamic dimensionless constant (K_e) is estimated from mathematical expression $K_e = \frac{1000 \times K_g \times M_{adsorbate} \times [adsorbate]^0}{\gamma}$

where K_g (L/mg) can be Langmuir, Sips, or other isotherms constant [35], $M_{adsorbate}$ is adsorbate molecular (or atomic) weight (g/mol), $[adsorbate]^0$ is standard concentration (1 mol L⁻¹), and γ is activity coefficient of sorbate which can be taken as unity in diluted solutions [51]. On the other hand, values of ΔS and ΔH can be estimated from the slope and intercept of plot of $\ln K_e$ (or equivalent expression) versus $1/T$, based upon $\ln K_e = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$ relation (Van't Hoff equation) [43,51,57]. The numerical value of Langmuir constant (b_M ; in Lmol⁻¹) is equal to K_e value [43,49,51], which was used in the above-mentioned Van't Hoff equation for thermodynamic calculations (Fig. 8b). The computed ΔG amounts at different temperatures of 288.15, 298.15, 308.15, and 318.15 K were -25.93, -27.26, -28.58, -29.97 kJmol⁻¹. The negative values lay the spontaneity of the process bare, and the more negative values at higher temperature reveal that sorption of ACN onto chitosan/MgO nanocomposite is more favorable at higher temperatures. The ΔH value of the process was 12.701 kJmol⁻¹, with which it can be claimed that a physisorption happened during the adsorption process [29]. The ΔS value was 134.12 which its positiveness represents the increase of randomness during the sorption process, which is perhaps due to the replacement of adsorbed waters with ACN molecules.

3.5. Kinetic properties

Kinetic properties of ACN sorption on the new sorbent was appraised by fitting the experimental data with various techniques. Such studies were conducted for identifying of the rate-controlling stage in the sorption process. As traditionally other workers do, firstly, the experimental data were fitted with by the pseudo first order (PFO) and pseudo second order (PSO) equations which have extensively been represented in sorption literature.

Visual goodness of fit can be observed in Fig. 9a, and the parameters computed for various initial concentrations and correlation coefficient (R^2) values have been reported in Table 3. In Table 3, along with the parameters and R^2 values, there are two statistical indices (χ^2 and Δq)

Table 2
Isotherm equations utilized for equilibrium investigations and the computed parameters and statistical indexes.

Mathematical relations	Isotherm name	Parameters			Statistical indices ^a		
$q_e = \frac{q_{\max} (K_S \cdot C_e)^{1/n}}{1 + (K_S \cdot C_e)^{1/n}}$	Sips isotherm	K^b	n	$q_{\max}^c$	χ^2	$\Delta q\%$	R^2
		0.358	1.045	120.101	0.224	4.805	0.9997
$q_e = \frac{q_{\max} K_T C_e}{[1 + (K_T C_e)^{n_1}]^{1/n}}$	Toth isotherm	K^d	n	$q_{\max}^c$	χ^2	$\Delta q\%$	R^2
		0.397	1.217	128.263	0.436	5.372	0.9988
$q_e = \frac{q_s b_K C_e}{(1 + b_K C_e)^{a_K}}$	Khan isotherm	K^d	n	$q_{\max}^c$	χ^2	$\Delta q\%$	R^2
		0.437	1.037	106.860	0.256	5.510	0.9997
$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^n}$	Redlich-Peterson isotherm	K^e	n	a	χ^2	$\Delta q\%$	R^2
		47.333	0.974	0.438	0.251	5.399	0.9997
$q_e = K_f C_e^{\frac{1}{n}}$	Freundlich isotherm	K^f	n		χ^2	$\Delta q\%$	R^2
		33.268		2.455	12.049	37.767	0.9524
$q_e = \frac{RT}{b} (\ln K_T C_e)$	Temkin isotherm	K^g		B	χ^2	$\Delta q\%$	R^2
		7.332		20.113	4.832	21.908	0.9877
$q_e = q_{DR} e^{-K_{DR} \mathcal{E}^2};$ $\mathcal{E} = RT \ln(1 + \frac{1}{C_e})$	Dubinin–Radushkevich isotherm	ϵ^h		q_0^c	χ^2	$\Delta q\%$	R^2
		0.197		94.475	47.111	58.561	0.9363
$q_e = \frac{Q_{\max}^0 + K_L C_e}{1 + K_L C_e}$	Langmuir isotherm	$q_{\max}^c$		b_L^e	χ^2	$\Delta q\%$	R^2
		116.882		0.390	0.287	5.808	0.9996

^a $\chi^2 = \sum_{i=1}^N \left(\frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}} \right)$; $\Delta q(\%) = 100 \sqrt{\frac{1}{N-1} \sum_{i=1}^N \left(\frac{q_{exp} - q_{cal}}{q_{exp}} \right)^2}$; and $R^2 = 1 - \frac{\sum (q_{e,exp} - q_{e,cal})^2}{\sum (q_{e,exp} - q_{e,mean})^2}$
^b L^n/g^n ,
^c mg/g,
^d mg/L,
^e L/mg,
^f $mg^{1-(1/n)} \cdot L^{1/n}/g$
^g L/g, and
^h $kJmol^{-1}$

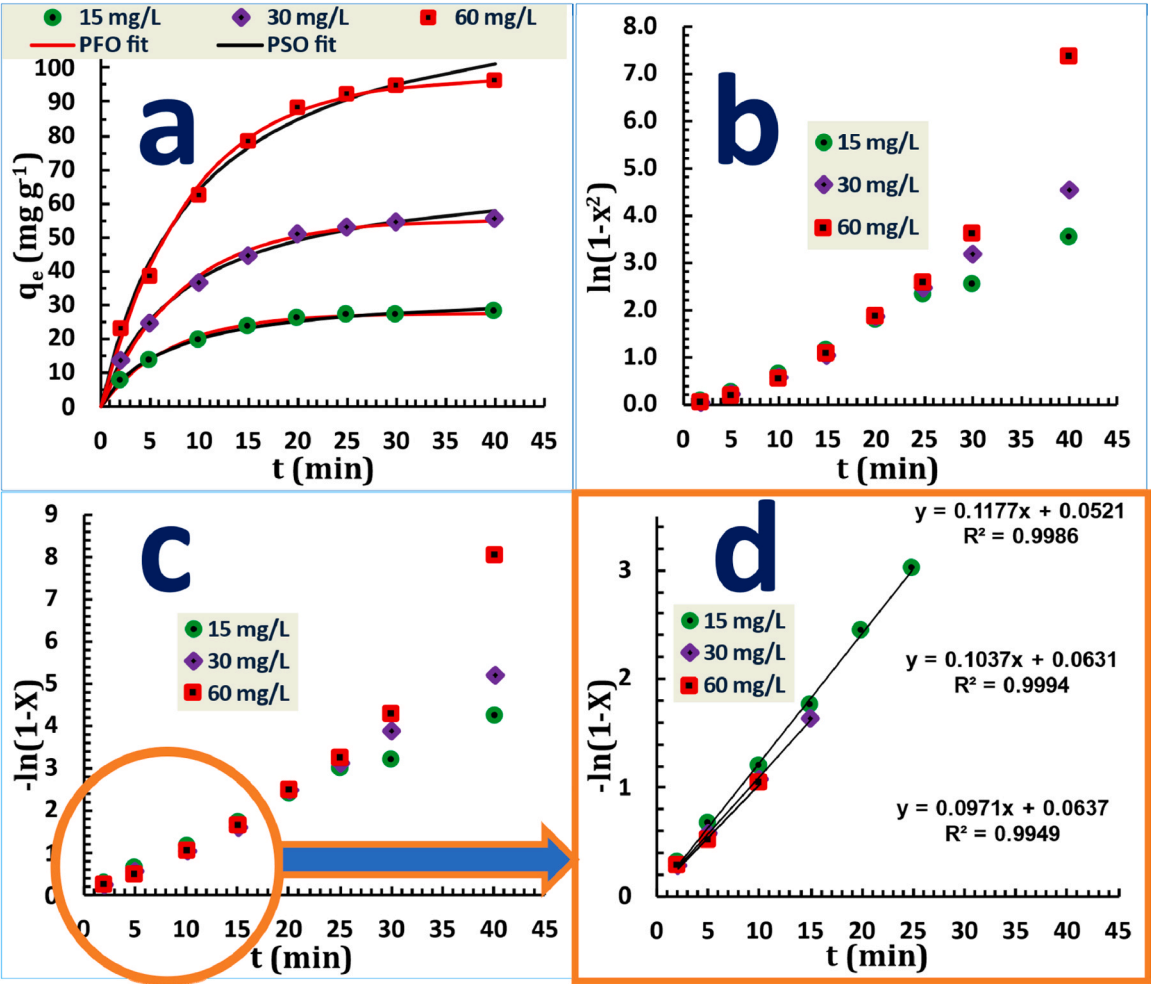


Fig. 9. Fitness of kinetic data with PSO and PFO models (a), Dumwald–Wagne model (b), and Boyd model (c and d).

Table 3

Mathematical relations utilized for kinetic evaluations and the calculated parameters and statistical indexes.

Mathematical relation	Model name	C ^a	Parameters	Statistical indices
$q_t = q_e \cdot [1 - \exp(-K_1 \cdot t)]$	PFO	15	k_1^b	q_e^c
		30	0.14	27.70
		60	0.12	55.50
$q_t = \frac{q_e^2 \cdot K_2 \cdot t}{[K_2 \cdot (q_e \cdot t) + 1]}$	PSO	15	k_2^d	q_e^c
		30	0.11	97.48
		60	4.16E-03	34.41
		15	1.62E-03	70.43
		30	8.35E-04	125.14
		60		1.06
				5.68
				0.9932
				0.9977
				0.9985
				0.9949
				0.9970
				0.9973

^a mg/L^b min⁻¹^c mg/g^d g/(mg.min)

which can be utilized for indication of the best fitted kinetic model. As the results reveal, one can not suggest that one of the two appraised kinetic models (PSO and PFO) has offered a better fit with the experimental data. For instance, although the $\Delta q\%$ values acquired for PSO model are smaller than those obtained for PFO model, PSO model failed to give good estimations of the q_e values. The experimental q_e values obtained at the initial ACN concentrations of 15, 30, and 60 mg/L were 28.7, 55.5, and 96.3 mg/g, respectively. As a matter of fact, the experimental q_e values are closer to those estimated by PFO model. Such outcomes disclose a rare case, which definitely needs more evaluations.

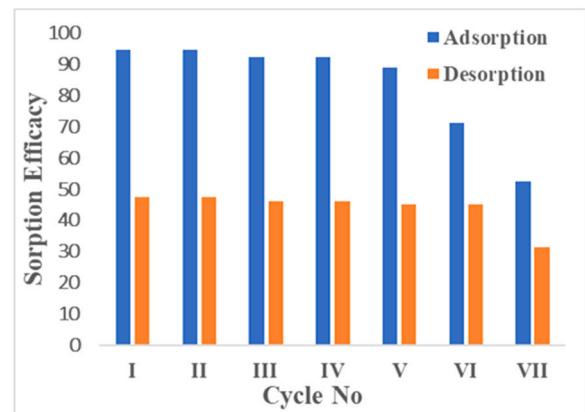
In order to find the possible role of intra-particle diffusion in ACN sorption control, experimental data were fitted with Dumas–Wagne intra-particle diffusion model which can be given as $-\ln(1-X^2) = Kt$ [65], where X (dimensionless) is the fraction of equilibrium attainment at any time (q_t/q_e ; sorption capacity at 't' time /equilibrium sorption capacity) and t (min) is time. As Fig. 9b displays, one can visually recognize that the plots of $-\ln(1-X^2)$ against t are not linear at all, and therefore intra-particle diffusion does not control the sorption rate of ACN on chitosan/MgO.

Further kinetic evaluations were accomplished by fitting Boyd's film diffusion kinetic model with the experimental data to find whether the film diffusion is the rate-controlling step in ACN sorption process. Boyd model can be represented as $-\ln(1-X) = Kt$ [65], where X (dimensionless) is the fraction of equilibrium attainment at any time (q_t/q_e ; sorption capacity at 't' time /equilibrium sorption capacity) and t (min) is time. Fig. 9c displays that Boyd's plots are not linear the whole range of sorption data, suggesting that the sorption process is not wholly controlled by the film diffusion.

Despite obtaining the above-mentioned results, the kinetic data should be inspected more closely. Adopting this strategy, the initial points of Fig. 9d can be inspected in a more attentive manner. Fig. 9d shows that film diffusion plays a major role in the initial stages of sorption process, since the Boyd's plots at the initial stages of sorption are linear with almost high correlation coefficients. Fig. 9d also shows that the role of film diffusion lingers more for the lower initial concentrations [20]. Such results reveal that the adsorption process is initially controlled by diffusion of ACN into the liquid film which is surrounded the sorbent particles. However, as the sorption process is progressed, the outside sites and the sites existing in wider pores are occupied with ACN molecules, and further adsorption needs the ACN molecules to diffuse into narrower pores [19,20]. Therefore, in the final stages of sorption process, the film diffusion loses its authority over the sorption process and the process will be controlled via a mixed mechanism of film and intra-particle diffusion which can be transformed to pure intraparticle diffusion in the last stages of the sorption process.

3.6. Regeneration of chitosan/MgO composite

The regenerative efficacy of such a composite is mandatory for predicting the adsorptive feasibility and efficiency. Hence, the reusable

**Fig. 10.** Plot for chitosan/MgO Regeneration.

nature of such CS/MgO composite was examined by performing out nearly 7 adsorptive/desorptive batch cycles. About 0.1 g of chitosan/MgO nanocomposite was agitated till the equilibrium with 50 mL of 50 mg/L of ACN solution.

Henceforth, ACN-loaded CS/MgO was filtered and rinsed with demineralized water to detach unadsorbed ACN molecules. Then ACN-loaded CS/MgO was blended with 0.5 M KOH to desorb ACN (10 mL). It was notified that the percentage sorption efficacy of such chitosan/MgO nanocomposite for the first two cycles was higher than 94.8 % and slightly further decremented to 92.37 % for 3rd and 4th cycles followed by a fall to 88.92 % for 5th cycle and later on reached to about 52.35 % for 7th cycle (Fig. 10). Henceforth, it can be possibly claimed that CS/MgO nanocomposite was remarkably favorable for ACN adsorption at least for 5 consecutive cycles.

3.7. Comparative analysis

Adsorption technology is a simple and cost-effective option for decontamination of waters and waste waters. In addition to simplicity and cost-effectiveness, this technology brings about high efficiency and, therefore, it is credited to be one of the most prominent technologies for removal of PAHs pollutants [55]. Until now, many low-cost and effective sorbents have been tested to remove ACN aqueous media.

Adsorbents like fatty acid mediated porous activated carbon [31], raw biomass [41], *pseudomonas* sp. Qian et al., [50], Triton X-100-facilitated biochar-immobilized *pseudomonas aeruginosa* [40], natural fiber [30], bacteria and fungi [37], etc. have been used for ACN removal from water media. With an adsorption capacity as high as 116.9 mg/g, compared with these mentioned adsorbents, the nanocomposite studied in the current work (chitosan/MgO) has the highest adsorption capacity for ACN removal from aqueous solutions. These results confirm the chitosan/MgO merits for application in ACN removal

Table 4
Comparing chitosan/MgO with other sorbents.

Components for Acenaphthene sequestration	Equilibrium sorptive capacity (mg/g)/efficiency %	References
Rice bran-biochar	2.570	Lu et al., 2018 [61]
Powdered rice bran	2.363	Lu et al., 2018 [67]
UiO-66	99.72	[67]
ZIF-8	60.71	[67]
Ultrasonic assisted activated carbon	52.74	Aravind et al., 2018
Steam initiated biochar	38.2	Sajjadi et al., 2018
Carbon nanotubes	145.96	[29]
Porous organic polymers	0.14	[14]
Chitosan/MgO composite	116.88	This work

plants (Table 4).

3.8. Acenaphthene adsorptive mechanism

Based on pH estimates, the chitosan/MgO composite is protonated and has positive charge on its surface at 5.5 pH. On the other hand, electron-rich structure of ACN molecules was pulled to positive surface of adsorbent, owing to the electrostatic attraction. This envisaged an increased ACN sorptive efficacy of the nanocomposite. Also, thermodynamic findings justified that ACN adsorption on to composite sorbent occurred via physisorption phenomena, which emphasizes the π interactions between ACN and composite surface.

4. Conclusion

In this study, the chitosan/MgO nanocomposite was synthesized and successfully used to remove Acenaphthene from aqueous solutions. The adsorbent (chitosan/MgO nanocomposites) displayed to be an excellent sorbent for removal of Acenaphthene, so that it showed high efficiency and its usage resulted up to almost 97 % Acenaphthene removal. The optimum conditions for the removal of Acenaphthene using chitosan-based nanocomposite was a dose of 50 mg at ambient temperature of 298 K, and an optimum pH of 5.5, which resulted in a removal efficiency of 93.95 %. The major adsorption capacity was achievable in approximately 50 min, which was higher from many adsorbents used for this purpose. The SEM analyses displayed that the porosity of the nanocomposite is high, and XRD results confirmed that the CS/MgO has a poor crystalline nature. FTIR analyses explained the functional groups present on the adsorbent. Langmuir equations along with some three-parameter models provided a good fit to the experimental outcomes with R^2 value greater than 0.9996. The result of the kinetic scrutinization indicates that neither pseudo second order nor pseudo first order kinetic model fitted with the data in the whole range. Further scrutinization of kinetic outcomes revealed the controlling effect of film diffusion in a vast range of contact time. The thermodynamic calculations revealed the feasibility and spontaneity of the adsorption process. Overall, the new composite was triumphally employed for removal of Acenaphthene from aqueous media and can be used for full-scale treatment plants after the further necessary investigations.

CRediT authorship contribution statement

Praveenkumar T R: Writing – review & editing, Writing – original draft, Formal analysis, Data curation, Conceptualization. **T. Sathish:** Writing – original draft, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Omirsarik Baigenzhenov:** Writing – original draft, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Gulnar K. Ziyayeva:** Project administration, Methodology, Investigation, Conceptualization. **D.J. Jayaprabakar:** Validation, Supervision, Methodology, Investigation,

Formal analysis, Data curation, Conceptualization. **Emad Makki:** Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Jayant Giri:** Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **D. Prabu:** Funding acquisition, Formal analysis, Conceptualization. **S. Sathish:** Writing – original draft, Methodology, Investigation, Conceptualization. **J.Aravind Kumar:** Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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