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Removal of agricultural wastewater pollutants by integrating two waste materials, fish scales and neem leaves, as novel potential adsorbent

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ABSTRACT

Only 2.5% of the world's water is fresh, despite the fact that water covers approximately 70% of the planet. This water is used for several recreational purposes and gets polluted by wastewater disposal directly into freshwater bodies. Effluents dispersed into water bodies could be from various sources like industries, households, and agricultural activities. These effluents comprise heavy metals and chemical wastes directly released into water bodies without treatment and could include major contaminants like nitrates, nitrites, ammonia and phosphates. The present study mainly focuses on removal of four significant pollutants from agriculture wastes, i.e., nitrates, nitrites, ammonia, and phosphates. These pollutants are removed using adsorbents via a process known as adsorption. Adsorbents used in the study are fish scales and neem leaves. Several studies have been carried out to measure the efficiency of adsorbents in the removal of contaminants. These studies include equilibrium studies, kinetic studies and isotherm studies. Based on a complete analysis and results obtained, 95% to 99% of contaminants can be removed effectively with an adsorbent dosage of 0.4 g (0.2 g of fish scale and 0.2 g of neem leaves powder), optimum pH of 6 and at 303 K constant temperature. The dosage variance stems from changing the dosages of two adsorbents in three ways, i.e., by taking both adsorbents in equal dosages, and increasing the dosage of one adsorbent compared to the other and vice versa. The contact time varied from 0 to 140 min and the Initial concentration of pollutants has also been varied from 30 to 70 mg/L. In addition to the above variations, thermodynamic studies were also done, and based on the negative values of ΔG and positive value of ΔH and ΔS, it is evident that the reaction of novel adsorbent (combination of fish scales and neem leaves) is spontaneous and endothermic.

Key words: adsorbent, adsorption, contaminants, fish scales, isotherm studies, kinetic studies

HIGHLIGHTS

- Agricultural wastewater pollutants causing eutrophication is one of the reasons for polluting the river bodies.
- These pollutants, i.e. nitrates, nitrites, ammonia and phosphates, were treated by integrating two waste materials, fish scales and neem leaves, as single adsorbent.
- About 95% to 99% of contaminants could be removed from the considered pollutant concentration.
- Kinetic and isotherm studies were also included in the study.

INTRODUCTION

The available freshwater resources are fast depleting with the daily increase in pollution following varied practices such as disposal of industrial effluents directly into the water without proper treatment and increase of fertilisers in agricultural practices impacting soil fertility (Pimentel *et al.* 2007). Wastewater that is disposed from agricultural fields contaminates water bodies due to pollutants such as nitrates, nitrites, ammonia and phosphates (Rao 2006). Different methods have been devised to remove pollutants from wastewater, of which adsorption method is considered one of the best methods, wherein low-cost adsorbents are used to remove pollutants (Lito *et al.* 2012). Excessive amounts of phosphates and nitrates in water can lead to eutrophication, which causes depletion of dissolved oxygen in water and results in pollution of water bodies. As per Indian Standard IS 10500-2012, the acceptable limit of nitrogen in the form of nitrates is 45 ppm as per Central Pollution Control

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Board (CPCB), the amount of nitrates in wastewater that is disposed is limited to 10 ppm; and according to CPCB, the permissible value for dissolved phosphates (as P) is 5 ppm (mg/L).

Different adsorbents have been taken into consideration for the removal of diverse heavy metals and pollutants from wastewater. Solid waste residue (SWR) from alum and the sulphuric acid factory has been used for the concurrent removal of nitrates and phosphates from wastewater. The results of the study showed that optimum contact time was 90 min and the adsorbent dose was 20 g/L. The R^2 values of 0.99 and 1.0 obtained from pseudo-second-order equation showed that this model fitted the adsorption kinetics. The adsorption of phosphate and nitrate was better examined using Freundlich and Langmuir isotherms, with R^2 values of 0.99 and 0.98 for phosphate and 0.99 and 0.96 for nitrate, respectively, according to isotherm studies. The SWR exhibited a low inclination towards nitrate adsorption (0.071 mg/g), while SWR's effectiveness in removing phosphate (0.962 mg/g) was decent within optimum contact time. Based on their studies, the SWR could remove phosphates from wastewater compared to nitrates under optimum conditions (Kang & Jeen 2021).

Fly ash is one waste byproduct that can be considered as an adsorbent and used effectively to eliminate anionic surfactants from wastewater. Studies showed that fly ash removed sodium dodecylbenzenesulfonate (SDBS) surfactants effectively at pH 2 at temperature 25 °C; and both physisorption and chemisorption were observed during adsorption of SDBS surfactants on to fly ash. Removal efficiency varied from 62.59% to 84.41% as SDBS concentrations were changed (Siyal *et al.* 2019).

Kinetic and isotherm studies are the essential studies incorporated to determine the adsorption capacity observed for different pollutants. Langmuir isotherm and second-order kinetic studies are conducted to study the affinity of bone char as adsorbent in Pb(II) removal from aqueous solution. When cellulose-modified bone char was used in place of bone char, uptake capacity of Pb(II) on to bone char increased from 89.9 to 115.7 mg/g (Liao *et al.* 2021).

Using rice husk ash as adsorbent, oxytetracycline was removed by varying pH, contact time and temperature. Equilibrium for removing of oxytetracycline was reached at 420 min for lower concentration (40 to 80 mg/L). Based on regression analysis, R^2 value of Langmuir isotherm was best suited for adsorption study of oxytetracycline on to rice husk ash (Andrade *et al.* 2020).

Several waste materials such as corn and rice husk biochar can be used as adsorbents for removal of select heavy metals, where removal efficiencies for different heavy metals are Fe (90%), Cr (65%) and Pb (90%) for biochar from rice husk, whereas removal efficiencies for corn husk biochars are Pb (slightly $>$35%), Cr (only 20%). The contact time for all biochars varies between 20 and 30 min (Sanka *et al.* 2020).

Fine powder prepared from mature neem leaves was used as an adsorbent to remove metal ions from water. A small amount of 1.6 g dm^{-3} neem leaves powder used as adsorbent could remove 87% of Cr(VI) at an optimum contact time of 300 min. Suitability of neem powder adsorbent was additionally tested with isotherms and equilibrium kinetic studies. Adsorption coefficients indicated high potentiality of neem leaf powder in removing Cr(VI) from water (Sharma & Bhattacharyya 2005).

In the current study, neem leaves and fish scales have been used for the elimination of different pollutants from wastewater. The main objective is to study the efficiency of fish scales and neem leaves as novel adsorbent to remove agricultural wastewater pollutants such as nitrates, nitrites, ammonia and phosphates. Adsorption capacities are investigated by altering the influence of adsorbent dosage, contact time, and pollutant concentrations (mg/L). Further analysis was carried out by studying the availability of biosorption capacity through kinetic suitability models such as pseudo-first-order and pseudo-second-order kinetics. The intensity of biosorption was studied using different isotherm studies such as Langmuir isotherm, Freundlich isotherm and Temkin isotherm (Nimibofa *et al.* 2017).

Novelty of this research article

The primary purpose of this research is to utilise a low-cost adsorbent to remove pollutants including nitrates, nitrites, phosphorus, and ammonia from agricultural wastewater. Many authors have employed various adsorbents to remove nitrates and phosphorus, but only a few have used novel adsorbents, which are a fusion of various adsorbents. The primary goal of this study is to determine the efficiency of a composite adsorbent, which is a combination of two individual adsorbents, fish scales and neem leaves powder, in removing four pollutants that are released directly into river bodies from untreated agricultural wastewater. Another critical aspect is the use of fish scales as an adsorbent to remove pollutants, particularly nitrates and phosphates, which cause eutrophication in river bodies if released in excess, which the authors have yet to investigate using fish scales.

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MATERIALS AND METHODOLOGY

Preparation of adsorbent

Fish scales

Waste fish scales were collected from the local fish market near Kakinada bus station, Kakinada, Andhra Pradesh, India. Using distilled water, these fish scales were thoroughly washed to remove unwanted particles and subsequently dried at 110 °C using a hot air oven. Dried fish scales were then ground with a mortar grinder, and pulverised scales in powder form were collected by sieving through a 1-mm sieve and retained on an 850 μm particle size sieve (Figure 1).

Neem leaves

Neem leaves were collected locally from Kakinada, Andhra Pradesh, India, and then washed using distilled water to remove unwanted particles. A hot air oven was used to dry the leaves, which were then ground with a mortar grinder. Neem powder was obtained by passing through a 1-mm sieve and retained on an 850 μm particle size (Figure 2).

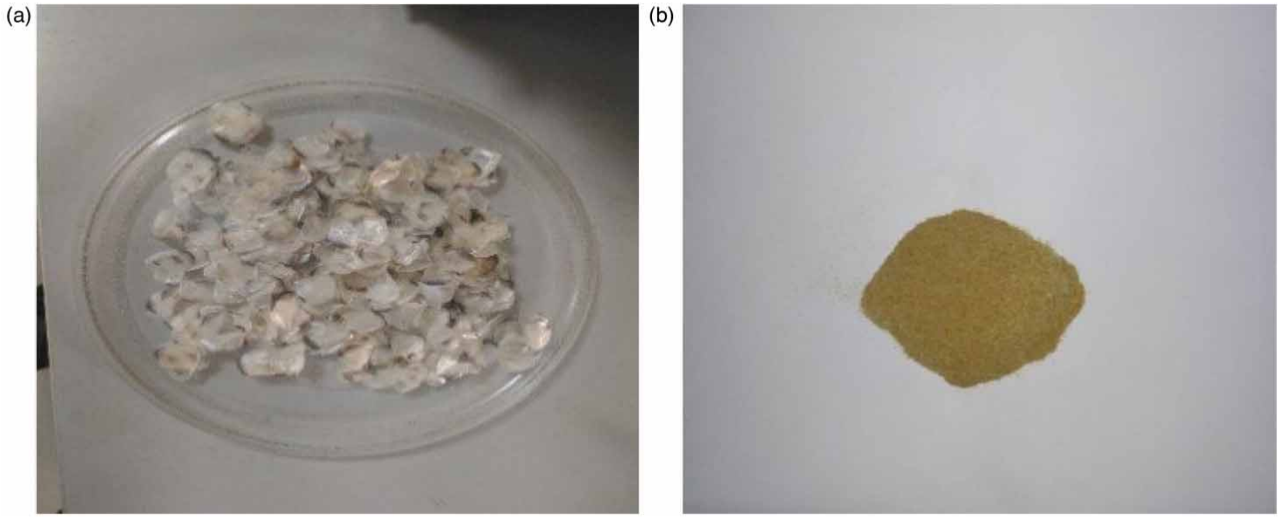

Figure 1 | (a) Fish scales and (b) fish scale powder.

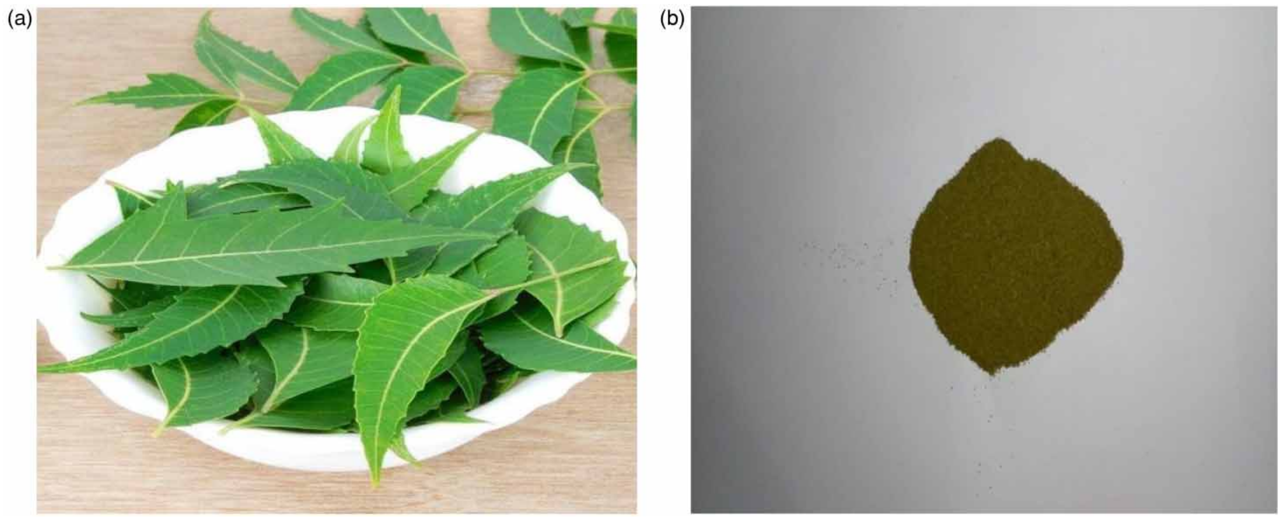

Figure 2 | (a) Neem leaves and (b) neem leaves powder.

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Preparation of adsorbate

Phosphate solution (stock) was prepared by dissolving a known amount of 0.439 g potassium dihydrogen orthophosphate (KH_2PO_4) in 1,000 mL distilled water. The desired solution (standard) was obtained by further diluting stock solution using distilled water. In similar manner, nitrate and nitrite stock solution was prepared by dissolving 0.7218 g of sodium nitrite salt ($NaNO_2$) and potassium nitrate salt (KNO_3) in 1,000 mL distilled water, respectively. The desired standard solutions of NO_3^- were obtained by diluting stock solution using distilled water; 0.7218 g ammonium chloride salt (NH_4Cl) was dissolved in 1,000 mL distilled water to make an ammonia solution (stock). The desired standard solution was obtained by further diluting stock solution using distilled water.

Equipment used for testing of pollutants

After passing the samples through filter paper, the concentrations of nitrate, nitrite, ammonia, and phosphate for each sample were determined using a HACH DR 3900 Laboratory Spectrophotometer for water analysis and a WENSAR UV Visible spectrophotometer, LMSP UV 1200.

EXPERIMENTAL PROCEDURE

In the first stage, the dosage of adsorbents was fixed as 0.4 g, of which fish scale powder and neem leaf powder were taken equally, i.e., 0.2 g each. The concentration of pollutants in the stock solution was maintained as 50 mg/L. Following the addition of adsorbent to a solution, the flasks were rotated at the rate of 165 rpm; and the uptake of pollutants was tested for different contact periods with 10-minute variation until uptake capacity became constant. The results for different pollutants were recorded accordingly.

In the second stage, the concentration of pollutants was varied from 30 to 70 mg/L, keeping the dosage of adsorbents as 0.4 g with fish scale powder and neem leaf powder taken equally. Flasks containing the solution were rotated at the rate of 165 rpm, and the uptake of pollutants was tested for optimum contact time and results were noted.

In the third stage, the amount of adsorbent was altered by changing the dosages in three ways, i.e., by taking both adsorbents in the same dosage (0.2 g each), by increasing the dosage of one adsorbent (0.3 g) and decreasing the dosage of the other adsorbent (0.1 g) and vice versa, and results obtained were recorded accordingly.

Based on the results obtained, further analysis was carried out using different isotherm studies to determine the effective bond between adsorbents and different pollutants. Different kinetic studies were carried out to determine final optimum conditions to implement in that actual scenario.

Equilibrium studies

The following three isotherm studies were used in order to determine the effective bond between adsorbents and different pollutants.

Langmuir isotherm

The Langmuir isotherm equation is given by

$$\frac{q_{eq}}{q_m} = \frac{bC_{eq}}{(1 + bC_{eq})} \tag{1}$$

where C_{eq} (mg L^{-1}) and q_m (mg/g) are the equilibrium molecule concentration and the amount of adsorbed molecules on the adsorbent surface at any given moment, respectively.

The above equation is written as

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{(bq_m)} + \frac{C_{eq}}{q_m} \tag{2}$$

By plotting a graph between C_{eq}/q_{eq} and C_{eq}, slope $(1/q_m)$ and intercept $(1/(bq_m))$ can be determined. Separation factor (R_L), which is given by $R_L = 1/(1 + bC_{eq})$, can be used for assessment of adsorbent on different pollutants.

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Freundlich isotherm

The Freundlich isotherm can be expressed as (Babu & Gupta 2008)

$$Q_{\mathrm{eq}} = K_f C_{\mathrm{eq}}^{1/m} \tag{3}$$

K_f represents the biosorption capacity of metal equilibrium concentration and 1/m represents a degree of biosorption with equilibrium concentration. For favourable biosorption, the value of m must be between 1 and 10 (Depci *et al.* 2012).

Taking logarithms on both sides, we get

$$\ln q_{\mathrm{eq}} = \ln K_f + \frac{1}{m} \ln C_{\mathrm{eq}} \tag{4}$$

Temkin isotherm

The Temkin isotherm can be expressed as

$$q_{\mathrm{eq}} = \frac{RT \ln(A_T C_{\mathrm{eq}})}{b_T} \tag{5}$$

The above equation is rewritten as

$$q_{\mathrm{eq}} = \left(\frac{RT}{b_T}\right) \ln(A_T) + \left(\frac{RT}{b_T}\right) \ln(C_{\mathrm{eq}}) \tag{6}$$

Kinetic studies

For kinetic theory, the experiment was conducted in batch studies under optimum conditions. The flasks were placed in an orbital shaker with a constant rotational speed of 165 rpm at constant room temperature and at different time intervals. Once shaking was completed, the conical flasks were filtered in a centrifuge and analysed for pollutant concentration. An extensive number of models have been developed with varying degrees of complexity to achieve pollutant adsorption kinetics. In the present work, pseudo-first-order and pseudo-second-order kinetics have been studied to analyse adsorption kinetics for given nitrate, nitrite, ammonia and phosphate using adsorbents.

Pseudo-first-order kinetic model

The pseudo-first-order kinetic model is given by (Katal *et al.* 2012)

$$\frac{dq_t}{dt} = k_1 (q_{\mathrm{eq}} - q_t) \tag{7}$$

where q_t (mg/g) is biosorption intensity at time t;
q_{eq} (mg/g) is biosorption intensity at equilibrium time;
$k_1(\mathrm{min}^{-1})$ is rate constant of first-order biosorption.

Applying boundary conditions, Integrating equation $q_t = 0$ at $t = 0$ and $q = q_t$ at $t = t$, the resultant equation becomes

$$\mathrm{Log}(q_{\mathrm{eq}} - q_t) = -k_1 t + \log q_{\mathrm{eq}} \tag{8}$$

A plot of log ($q_{eq} - q_t$) vs t will be straight line with k_1 as slope and $\log q_{eq}$ as intercept.

Pseudo-second-order kinetics

The pseudo-second-order kinetic model (Kaparapu & Krishna Prasad 2018) is given by

$$\frac{dq_t}{dt} = k_2 (q_{\mathrm{eq}} - q_t)^2 \tag{9}$$

where k_2 is rate constant for pseudo-second-order system

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Applying boundary conditions $q_t = 0$ at $t = 0$ and $q = q_t$ at $t = t$;

$$\frac{t}{q_t} = \frac{1}{q_{eq}}(t) + \frac{1}{(k_2 q_{eq}^2)} \tag{10}$$

Thermodynamic study

The thermodynamic study is given by

$$\Delta G = RT \ln K_L \tag{11}$$

where R is the molar gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature in Kelvin, ΔG° (KJ/mol) is the Gibbs free energy change, enthalpy change ΔH° (KJ/mol), change in entropy ΔS° (KJmol^{-1} K^{-1}), and K_L (L/mg) is the constant.

Values of ΔH and ΔS are determined from the slope and intercept of a plot of lnK_L against 1/T (Mudzielwana *et al.* 2019). Similarly, K_L is given by

$$K_L = \frac{Q_{eq}}{C_{eq}} \tag{12}$$

where
Q_{eq} = equilibrium adsorption capacity of pollutant in mg/g
C_{eq} = equilibrium pollutant concentration in the solution (mg/L) (Mutavdžić Pavlović *et al.* 2017)

$$\Delta G = \Delta H - T\,\Delta S \tag{13}$$

RESULTS AND DISCUSSION

Effect of contact time

The effect of contact time was analysed by shaking 0.4 g of given adsorbents, i.e., mixture of powders of 0.2 g fish scales and 0.2 g neem leaves, in 200 mL of nitrate, nitrite, ammonia and phosphate solution concentration 50 mg/L. This operation was carried out for different time intervals, like 10, 20, 30, 40, up to 140 min, at a speed of 165 rpm (Zhang *et al.* 2009). Following every time interval, the sample was analysed to calculate the amount of nitrate, nitrite, ammonia and phosphate. Figure 3

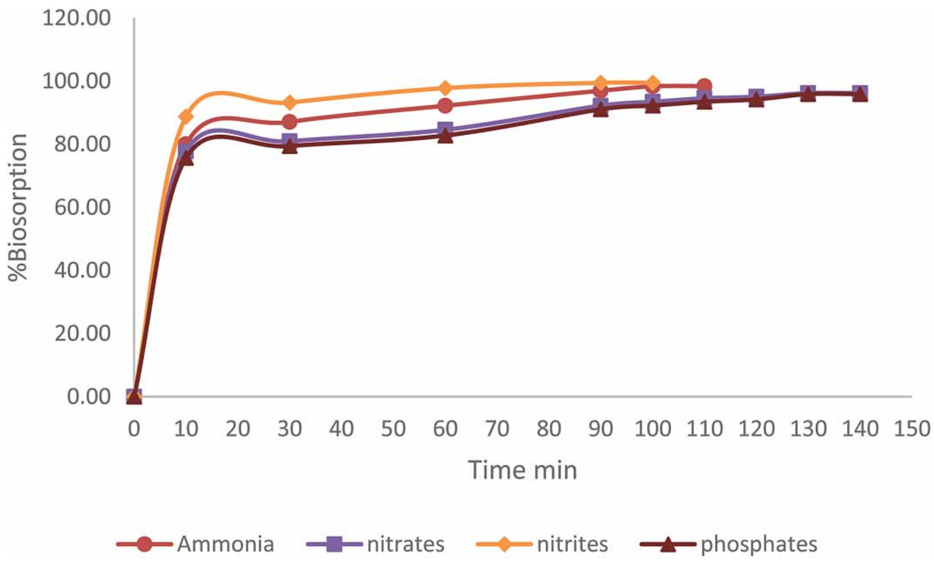

Figure 3 | Pollutant biosorption values at various time intervals. (Initial concentration = 50 ppm, adsorbent dose = 0.2 g/200 mL pollutant solution, temperature = 30 °C, pH = 6, Orbital shaking speed = 165 rpm).

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shows % biosorption capacities at different time intervals. As the time interval increased, the adsorption capacities for the different pollutants also increased, and Table 1 shows the % biosorption capacities at optimum contact time. It can also be observed that % biosorption for nitrites is greater, followed by ammonia, nitrate and phosphate. It can be concluded that the removal affinity of adsorbents is greater for nitrites, ammonia, nitrate and phosphate. Similar results were also observed, i.e. the increase of adsorption capacity of Cr(VI) in the removal of Cr(VI) from an aqueous solution, where the contact time is varied from 10 to 70 min (Panda *et al.* 2017).

Effect of adsorbent dose

50 m/L nitrate, nitrite, ammonia and phosphate solutions, each of 200 mL, with an equal amount of adsorbent dosage of 0.4 g, while dosage variance came from changing dosages of two adsorbents in three ways, i.e., by taking both adsorbents in equal dosage and by taking one adsorbent in greater dosage and the other adsorbent in lesser dosage and vice versa, and agitated with constant agitation speed at 165 rpm for equilibrium time at constant temperature (Wei *et al.* 2008). The concentration of nitrate, nitrite, ammonia and phosphate for each individual sample was determined. From Figure 4 and Table 2, it can be concluded that when the dosage of adsorbent of fish scales is 0.3 g and that of neem leaves is 0.1 g, the capacity for removal of pollutants gets increased as compared to the remaining two cases, and the order of % removal is nitrites, followed by ammonia, phosphates and nitrates. Previous research has shown that the increase in the adsorbent

Table 1 | % Biosorption for different pollutants at optimum contact time

Pollutant	Contact time in min	% of biosorption
Nitrate	140	96.24
Nitrite	100	99.5
Phosphate	140	95.92
Ammonia	110	98.42

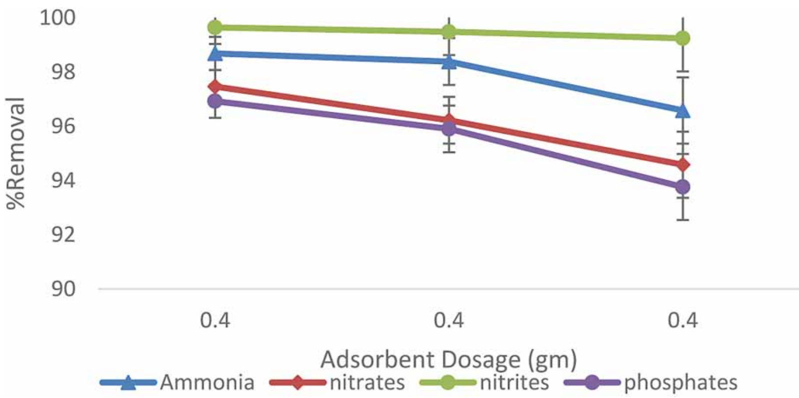

Figure 4 | Effect of dosage variance on % removal of different contaminants. (Initial concentration = 50 ppm, temperature = 30 °C, pH = 6, orbital shaking speed = 165 rpm.) Error bars represent the standard deviation of the mean.

Table 2 | Effect of dosage variance on % biosorption of different pollutants

Dosage of fish scale powder (g)	Dosage of neem powder (g)	Total dosage of both fish scale and neem leaf powder (g)	Ammonia	Nitrates	Nitrites	Phosphates	Standard error
0.3	0.1	0.4	98.68	97.46	99.64	96.92	0.6
0.2	0.2	0.4	98.38	96.22	99.48	95.90	0.9
0.1	0.3	0.4	96.58	94.58	99.24	93.76	1.2

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dose can increase the % biosorption capacity. For example, lead(II) removal using Polypyrrole-Based Activated Carbon has obtained similar results in that an increase in the adsorbent dosage improved the adsorption capacity (Alghamdi *et al.* 2019). However, in this study the adsorbent dosage is the same (0.4 g), but variations of the two adsorbents are made as shown in Table 2, which showed that the dosage of fish scales has more effect than that of neem leaves on the % removal of pollutants is more. From this it is evident that the efficiency of fish scales is more than that of neem leaves in removing pollutants. However, the combination of both showed better results.

Effect of initial pollutant concentration (Co)

Different pollutant concentrations of 30, 40, 50, 60 and 70 mg/L (Ahmed *et al.* 2010), 200 mL of each, were transferred to 250 mL conical flasks. Subsequently, 0.4 g of fish scale powder and neem leaf powder in equal dosages (0.2 g/L) was added to each of those beakers. The beakers were kept under rotation at 165 rpm for optimum contact time at room temperature. Collected samples were passed through filter paper and tested for concentrations of nitrate, nitrite, ammonia and phosphate present in aqueous solution. From Figure 5 and Table 3, it can be deduced that when the initial concentration of pollutants was varied from 30 to 70 ppm, the adsorbent's efficiency decreased for a constant adsorbent dosage of 0.4 g. The decrease of the adsorption capacity with an increase in the pollution concentration can be validated by Katal *et al.* (2012). As the pollutant concentration rises from 50 to 300 mg/L, the adsorption capacity decreases from 94.5% to 46.3%.

Effect of pH

The surface charge of the biosorbent material and the degree of ionisation of the pollutant are affected by an aqueous solution's pH, a vital monitoring parameter in biosorption. In this research the removal efficiencies of nitrates, nitrites, phosphates and ammonia biosorption data were determined and obtained in the pH range of 2 to 9 (Abdus-Salam & Adekola 2005) with $C_0 = 50$ mg/L, along with 0.4 g of integrated biosorbent (0.2 g of each, i.e. fish scales and neem leaves powder). Figure 6 and Table 4 depict the influence of aqueous solution pH on the % biosorption of several contaminants along with the error bars. The % biosorption of the nitrates, nitrites and ammonia has shown a significant increase when pH value is varied between 2 and 6, and it is also seen that there is a decrease in the % biosorption after pH 6 in reference to

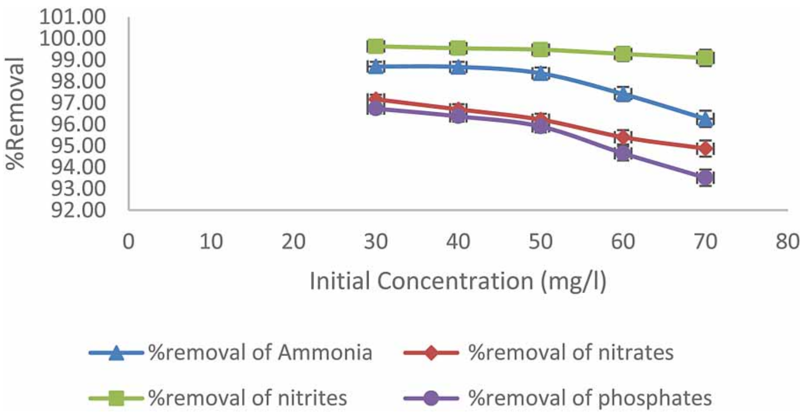

Figure 5 | Effect of varying concentrations of different pollutants. (Adsorbent dose = 0.2 g/200 mL pollutants solution, temperature = 30 °C, pH = 6, Orbital shaking speed = 165 rpm). Error bars represent the standard deviation of the mean.

Table 3 | Effect of adsorbent on different pollutants with variations in initial pollution concentration

Initial pollutant concentration	% removal of nitrates	% removal of nitrites	% removal of ammonia	% removal of phosphates	Standard error
30	97.17	99.63	98.70	96.73	0.2
40	96.70	99.55	98.68	96.38	0.2
50	96.22	99.48	98.38	95.90	0.3
60	95.40	99.28	97.42	94.65	0.3
70	94.87	99.10	96.26	93.51	0.4

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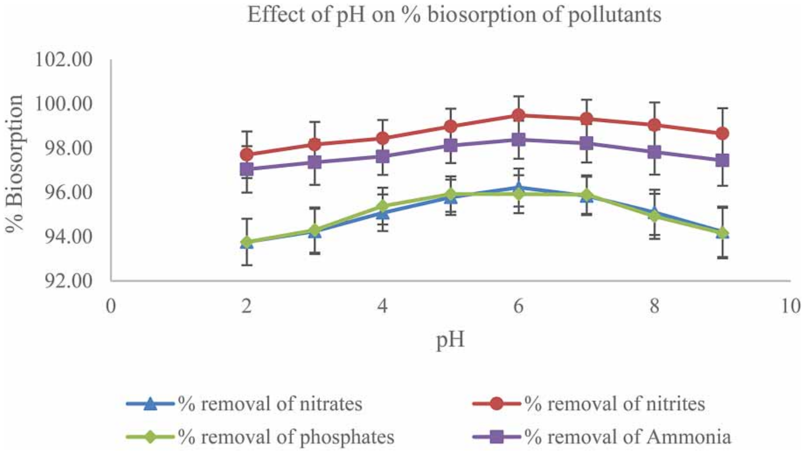

Figure 6 | Effect of pH on different pollutants. (Adsorbent dose = 0.2 g/200 mL pollutants solution, initial concentration = 50 ppm, temperature = 30 °C, orbital shaking speed = 165 rpm). Error bars represent the standard deviation of the mean.

Table 4 | Effect of pH on % removal of different pollutants

pH	% removal of nitrates	% removal of nitrites	% removal of phosphates	% removal of ammonia	Standard error
2	93.76	97.70	93.76	97.04	1.1
3	94.24	98.16	94.30	97.36	1.0
4	95.08	98.44	95.38	97.62	0.8
5	95.78	98.98	95.92	98.12	0.8
6	96.22	99.48	95.92	98.38	0.9
7	95.84	99.32	95.9	98.22	0.9
8	95.1	99.04	94.92	97.82	1.0
9	94.22	98.66	94.16	97.44	1.1

Figure 8 and Table 4. This result is comparable to adsorptive nitrate removal using red mud at pH 7, and beyond that pH value the % biosorption decreased (Cengeloglu *et al.* 2006), and on the contrary, as shown in Figure 8, the maximum % biosorption capacity for both the phosphates and nitrates is observed in the pH range from 5 to 7, and the pH value less than 4 and pH value greater than 7 did not show maximum % biosorption removal.

Effect of temperature

The effects of changes in the temperature on different pollutant uptake are shown in Figure 7, which along with Table 5 represents the biosorption of nitrates, nitrites, phosphates and ammonia by the combination of fish scales and neem leaves powder as a novel adsorbent. From the research it is evident that when the temperature was raised, the biosorption capacity increased. The temperature was investigated in batch experiments carried out at five constant temperatures: 298, 303, 308, 313 and 318 K (Jiang *et al.* 2018). With an increase in temperature, the % removal was increased from 95.04% to 97.36% for nitrates, 99.16% to 99.82% for nitrites, 97.96% to 99.34% for ammonia and 94.76% to 97.04% for phosphates for initial pollutants concentration of 50 mg/L. Because of the chemical interaction between biosorbates and biosorbents, and the increased rate of intra-particle diffusion, we can conclude that the biosorption reaction is endothermic (Gouamid *et al.* 2013).

Thermodynamic studies

To determine the applicability of fish scales and neem leaves as a novel adsorbent for the removal of nitrates, nitrites, ammonia and phosphates, the thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy change (ΔH), and entropy change (ΔS) are used to investigate the adsorption thermodynamics. These parameters ΔG, ΔH, and ΔS can be calculated using Equations (11) and (13), and the values of ΔH and ΔS are calculated using the slope and intercept of a plot of $\ln K_L$ against 1/T. Table 6 provides the values of ΔG at different temperatures for different pollutants with fish scales and neem

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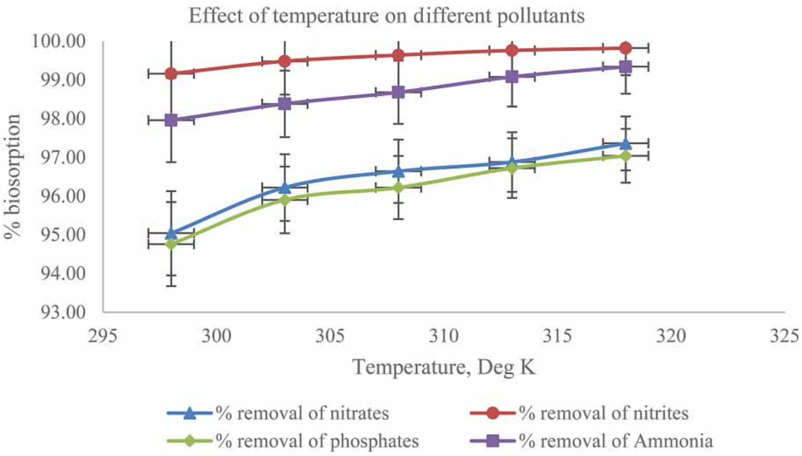

Figure 7 | Effect of Temperature on different pollutants. (Adsorbent dose = 0.2 g/200 mL pollutants solution, initial concentration = 50 ppm, pH = 6, orbital shaking speed = 165 rpm). Error bars represent the standard deviation of the mean.

Table 5 | Effect of temperature variations on % removal of different pollutants

Temperature (K)	% removal of nitrates	% removal of nitrites	% removal of phosphates	% removal of ammonia	Standard error
298	95.04	99.16	94.76	97.96	1.09
303	96.22	99.48	95.90	98.38	0.86
308	96.64	99.64	96.22	98.68	0.82
313	96.88	99.76	96.72	99.08	0.77
318	97.36	99.82	97.04	99.34	0.70

Table 6 | Thermodynamic parameters of nitrates, nitrites, ammonia and phosphates

Pollutant	Temp (K)	K_L	ΔG (KJ mol^{-1})	ΔH (KJ mol^{-1})	ΔS (JK^{-1} mol^{-1})	R^2
Nitrates	298	9.581	−5.599	23.830	99.233	0.9559
	303	12.728	−6.408			
	308	14.381	−6.827			
	313	15.526	−7.137			
	318	18.439	−7.705			
Nitrites	298	59.024	−10.103	61.06	239.143	0.9958
	303	95.654	−11.489			
	308	138.389	−12.624			
	313	207.833	−13.888			
	318	277.278	−14.872			
Ammonia	298	24.010	−7.875	44.93	176.747	0.9822
	303	30.364	−8.598			
	308	37.379	−9.273			
	313	53.848	−10.373			
	318	75.258	−11.424			
Phosphates	298	9.042	−5.455	22.45	94.056	0.9692
	303	11.695	−6.195			
	308	12.728	−6.514			
	313	14.744	−7.002			
	318	16.392	−7.394			

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leaves powder as a novel adsorbent, and Figure 8(a)–8(d) exhibits the graphs of lnK_L against 1/T. The negative value (ΔG) for all the four pollutants denotes that nitrates, nitrites, ammonia and phosphates adsorption on to the fish scales and neem leaves powder as a novel adsorbent is spontaneous and favourable (Rincón-Silva *et al.* 2016). Enthalpy change (ΔH) is positive, indicating that the adsorption of nitrates, nitrites, ammonia and phosphates was endothermic (Doke & Khan 2013). The entropy change (ΔS) value is also positive, suggesting that the ions of nitrates, nitrites, ammonia, and phosphates are dispersed randomly over the adsorbent surface (Manoj Kumar Reddy *et al.* 2013).

Adsorption isotherms

Langmuir isotherm

The Langmuir isotherm is explained in Figure 9(a)–9(d), where the graph was produced between C_{eq} and C_{eq}/Q_{eq}. It can be concluded that there is an effective link between adsorbent and various contaminants based on the Langmuir constant (b) values of nitrates, nitrites, ammonia, and phosphates. Constant b values declined in the following order: nitrites, ammonia, phosphates, and nitrates, as shown in Table 7. Table 7 also shows that the maximum adsorption capabilities ranged from 41.84 to 54.34 mg/g. It can be extrapolated from this that when the value of b increased, the percentage of pollutants eliminated increased.

Freundlich isotherm

It can be shown that values of the Freundlich constant (K_f), which represent biosorption capacities of different pollutants, reduced in the following order: nitrites, ammonia, phosphates, and nitrates, as shown in Table 8. From this, it can be determined that as the K_f value increased, so did the percentage of contaminants. The Freundlich constant M values in Table 8 range from 1.77 to 2.48, indicating that adsorption is favourable in these conditions. The value of M must be between 1 and 10 for good biosorption.

Temkin isotherm

The Temkin isotherm parameters for different pollutants, i.e., nitrates, nitrites, ammonia and phosphates, and their relation are shown in Figure 11(a)–11(d), and Table 9 shows the Temkin constants AT and BT values. Based on isotherm studies and from values of linear regression coefficients (R^2), it can be concluded that the Langmuir model is best suited for biosorption studies for the various pollution concentrations.

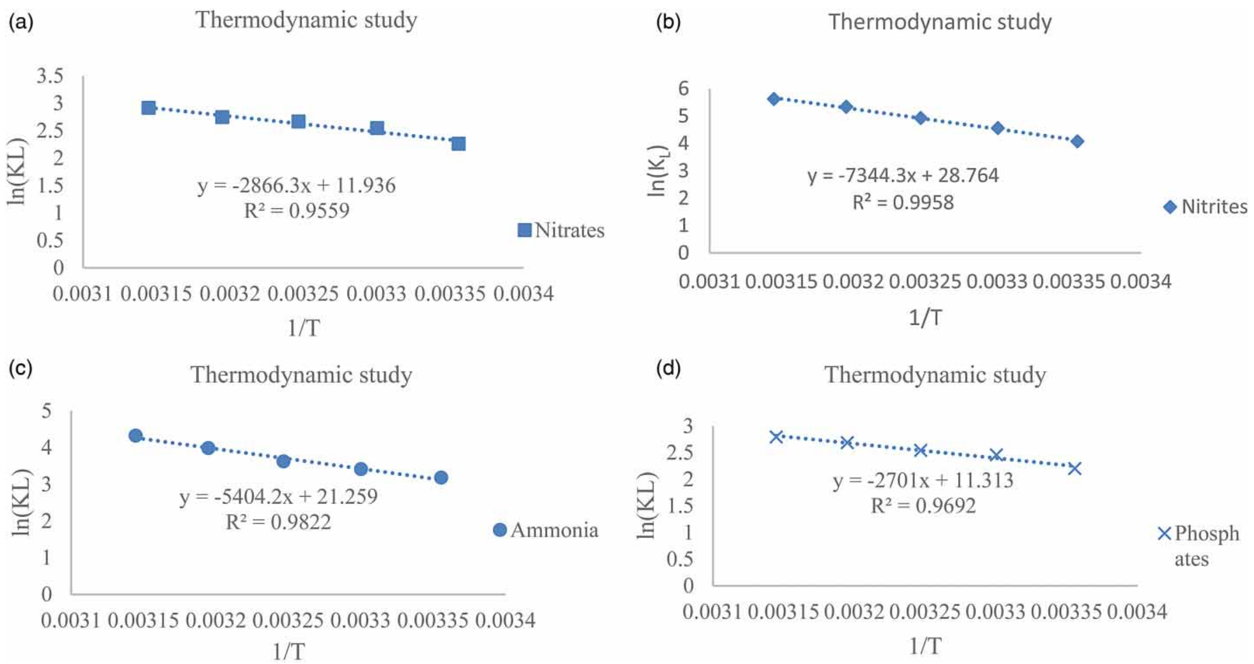

Figure 8 | (a)–(d): Plot between ln(K_L) vs 1/T for two different adsorbents. (Adsorbent dose = 0.4 g/200 mL pollutants solution, initial concentration = 50 ppm, pH = 6, orbital shaking speed = 165 rpm).

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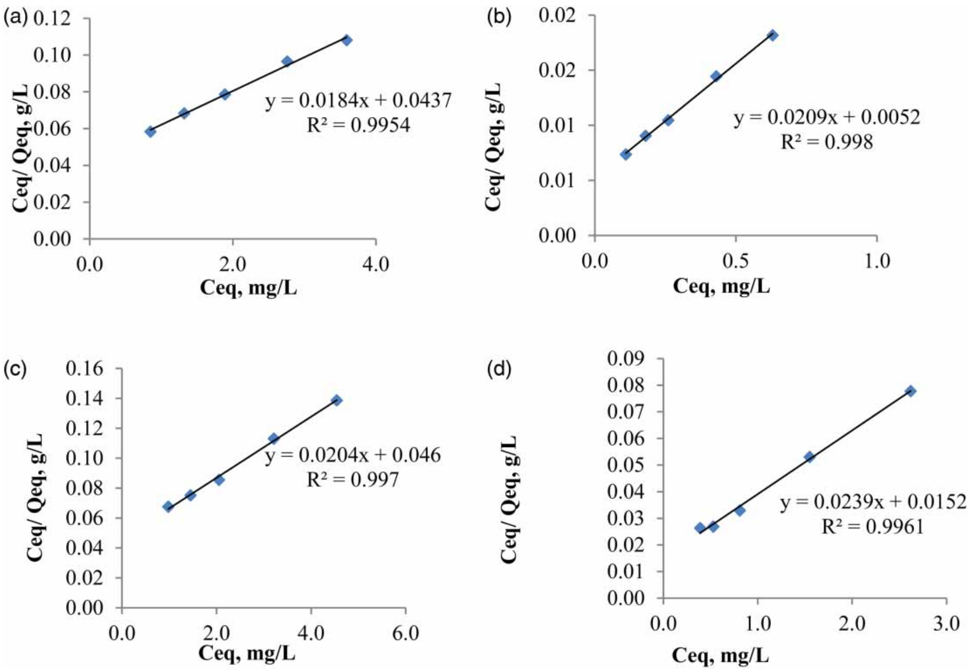

Figure 9 | (a)–(d) Langmuir isotherm graph for % biosorption of nitrates, nitrites, phosphates and ammonia.

Table 7 | Langmuir isotherm parameters

Pollutant	Equation	Q_{max} (mg/g)	b, L/mg	R^2
Nitrate	$(C_{eq}/Q_{eq}) = 0.0184\ C_{eq} + 0.0437$	54.34	0.421	0.9954
Nitrite	$(C_{eq}/Q_{eq}) = 0.0209\ C_{eq} + 0.0052$	47.84	4.019	0.998
Phosphate	$(C_{eq}/Q_{eq}) = 0.0204\ C_{eq} + 0.046$	49.01	0.443	0.997
Ammonia	$(C_{eq}/Q_{eq}) = 0.0239\ C_{eq} + 0.0152$	41.84	1.572	0.9961

Table 8 | Freundlich isotherm parameters

Pollutant	Equation	K_f (mg/g)	M	R^2
Nitrate	$\log Q_{eq} = 0.5651 \log C_{eq} + 1.2124$	16.30	1.77	0.996
Nitrite	$\log Q_{eq} = 0.4784 \log C_{eq} + 1.6499$	44.64	2.09	0.9861
Phosphate	$\log Q_{eq} = 0.5206 \log C_{eq} + 1.1894$	15.466	1.92	0.9778
Ammonia	$\log Q_{eq} = 0.4034 \log C_{eq} + 1.3835$	24.18	2.48	0.9318

Adsorption kinetics

Pseudo-first-order kinetic model

Based on values of rate constant K_1 from Table 10 and linear regression coefficient R^2 values from Figure 12(a)–12(d), it can be concluded that first-order kinetics is not best suited for the study of suitability for removal of different pollutants using adsorbents when compared with values of second-order kinetics.

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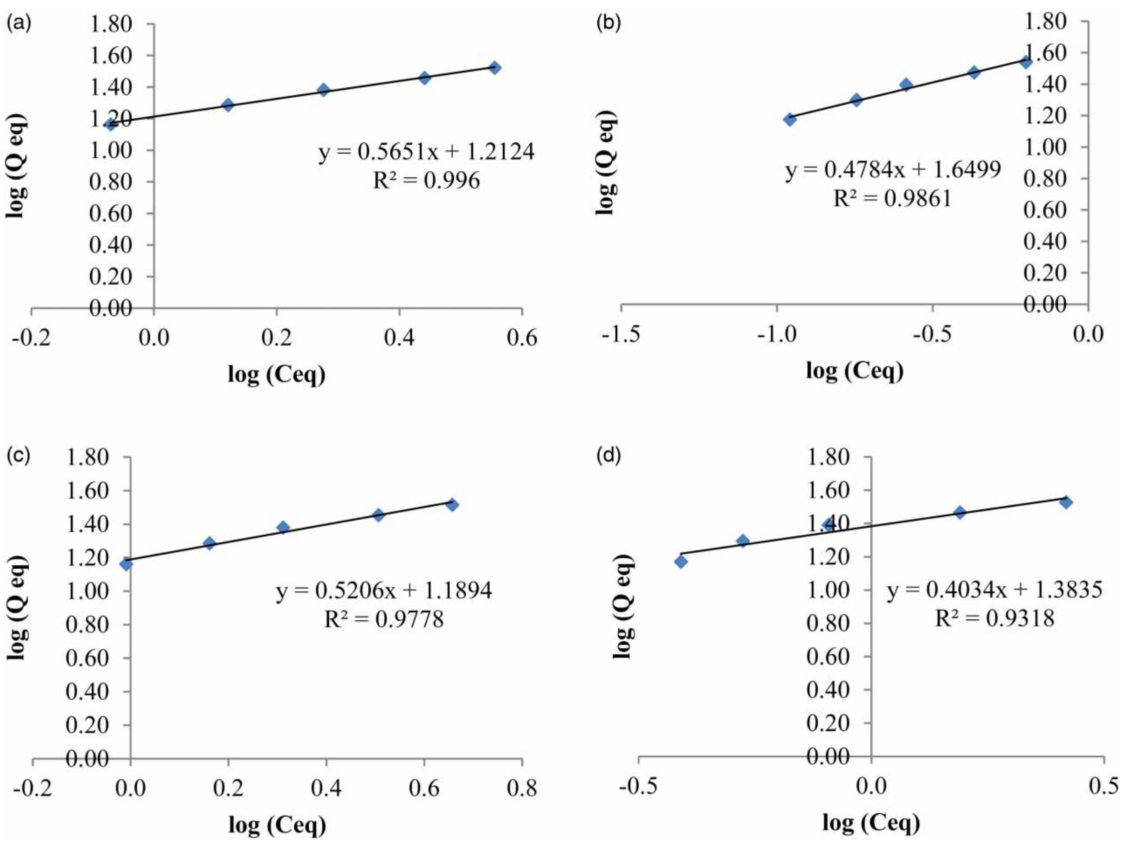

Figure 10 | (a)–(d) Freundlich isotherm graph for % biosorption of nitrates, nitrites, phosphates and ammonia.

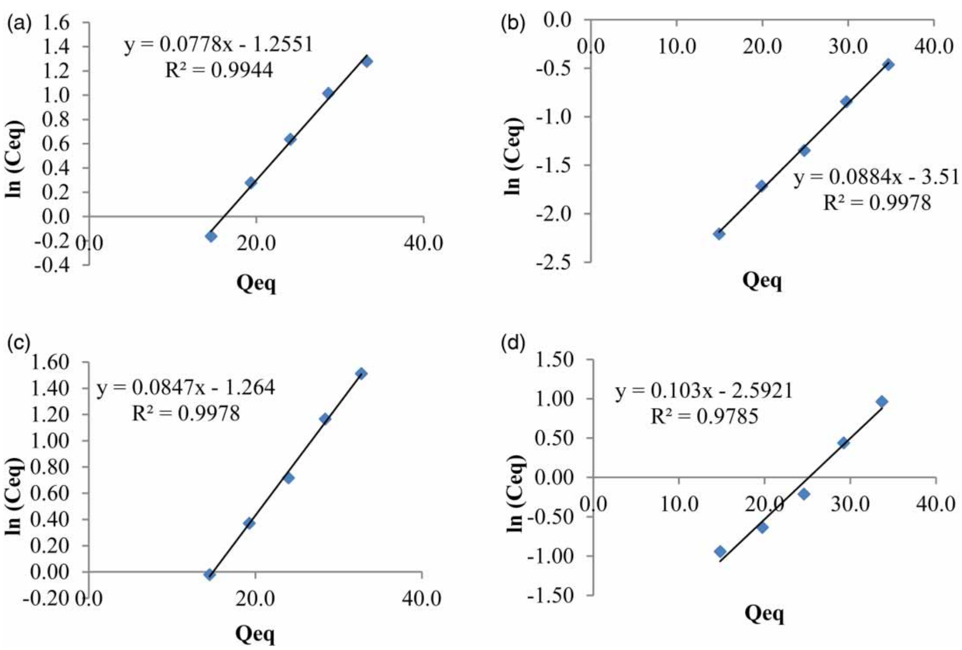

Figure 11 | (a)–(d) Temkin isotherm graph for % biosorption of nitrates, nitrites, phosphates and ammonia.

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Table 9 | Temkin isotherm parameters

Pollutant	Equation	A_T, L/mg	b_T, J/mg	R^2
Nitrate	$Q_{eq} = 0.389 \ln C_{eq} - 1.2551$	0.939	32,371.91	$R^2 = 0.9944$
Nitrite	$Q_{eq} = 0.4418 \ln C_{eq} - 3.510$	0.975	28,497.08	$R^2 = 0.9978$
Phosphate	$Q_{eq} = 04235 \ln C_{eq} - 1.264$	0.935	29,741.94	$R^2 = 0.9978$
Ammonia	$Q_{eq} = 0.5151 \ln C_{eq} - 2.5921$	0.961	24,457.69	$R^2 = 0.9785$

Table 10 | First-order equation and coefficients

Kinetics	Pollutant	Model equation	R^2	Rate constant, K_1
First-order	Nitrate	$\log(Q_{eq} - Q_t) = -0.0251$ t–1.4886	0.7402	0.0578 min^{-1}
First-order	Nitrite	$\log(Q_{eq} - Q_t) = -0.0354$ t–1.2572	0.8225	0.0851 min^{-1}
First-order	Phosphate	$\log(Q_{eq} - Q_t) = -0.025$ t–1.5375	0.7163	0.0575 min^{-1}
First-order	Ammonia	$\log(Q_{eq} - Q_t) = -0.0307$ t–1.4067	0.7862	0.0707 min^{-1}

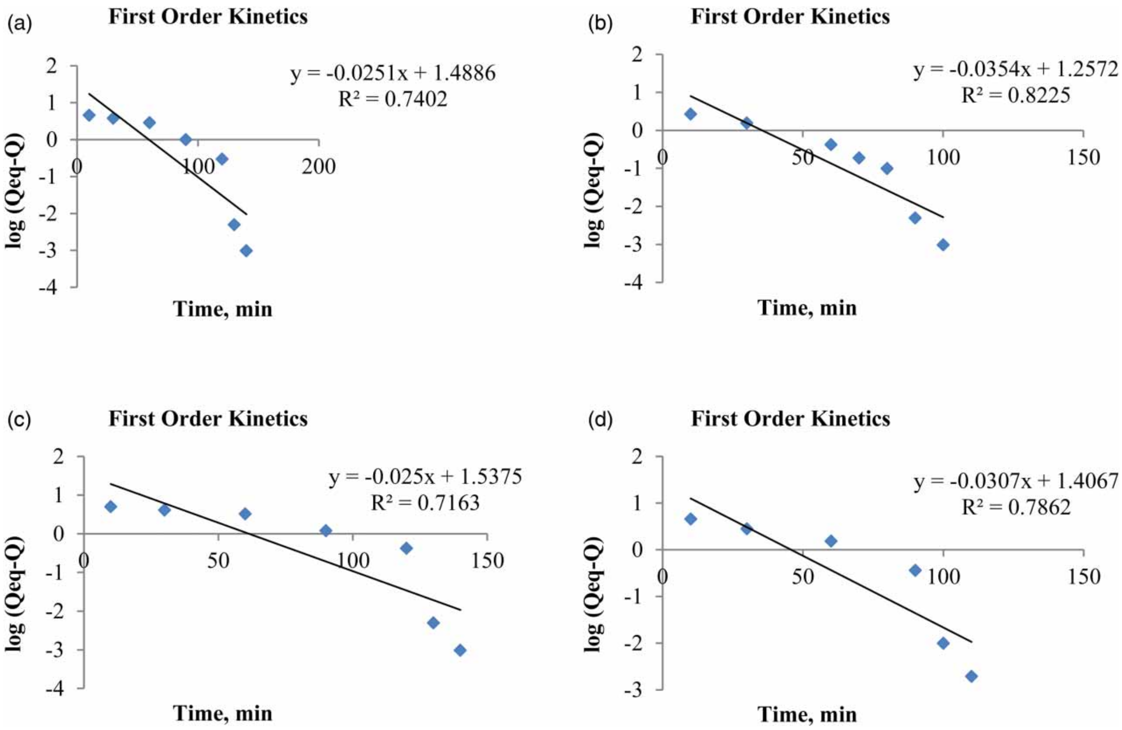

Figure 12 | (a)–(d) First-order adsorption kinetics of nitrates, nitrites, phosphates and ammonia.

Pseudo-second-order kinetic model

Based on tabulated values from Table 11 of rate constant (K_2), it can be observed that values of constant K_2 increased in the following order, i.e., nitrites, ammonia, phosphates and nitrates. From this, it can be deduced that as the K_2 value grew, the percentage of contaminants removed increased. From the R^2 values from Figure 13(a)–13(d), it may be stated that second-order kinetics is the best fit for describing the kinetic investigations of four different contaminants using novel adsorbents (combination of fish scales and neem leaves).

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Table 11 | Second-order equation and coefficients

Kinetics	Pollutant	Model equation	R^2	Rate constant, K_2
Pseudo-second-order	Nitrate	$t/Q_t = 0.04\ t + 0.2567$	0.9976	0.0062 g.(mg.min)$^{-1}$
Pseudo-second-order	Nitrite	$t/Q_t = 0.0985\ t + 0.1968$	0.9999	0.0197 g.(mg.min)$^{-1}$
Pseudo-second-order	Phosphate	$t/Q_t = 0.1001\ t + 0.7262$	0.9967	0.0055 g.(mg.min)$^{-1}$
Pseudo-second-order	Ammonia	$t/Q_t = 0.0983\ t + 0.4199$	0.9990	0.0092 g.(mg.min)$^{-1}$

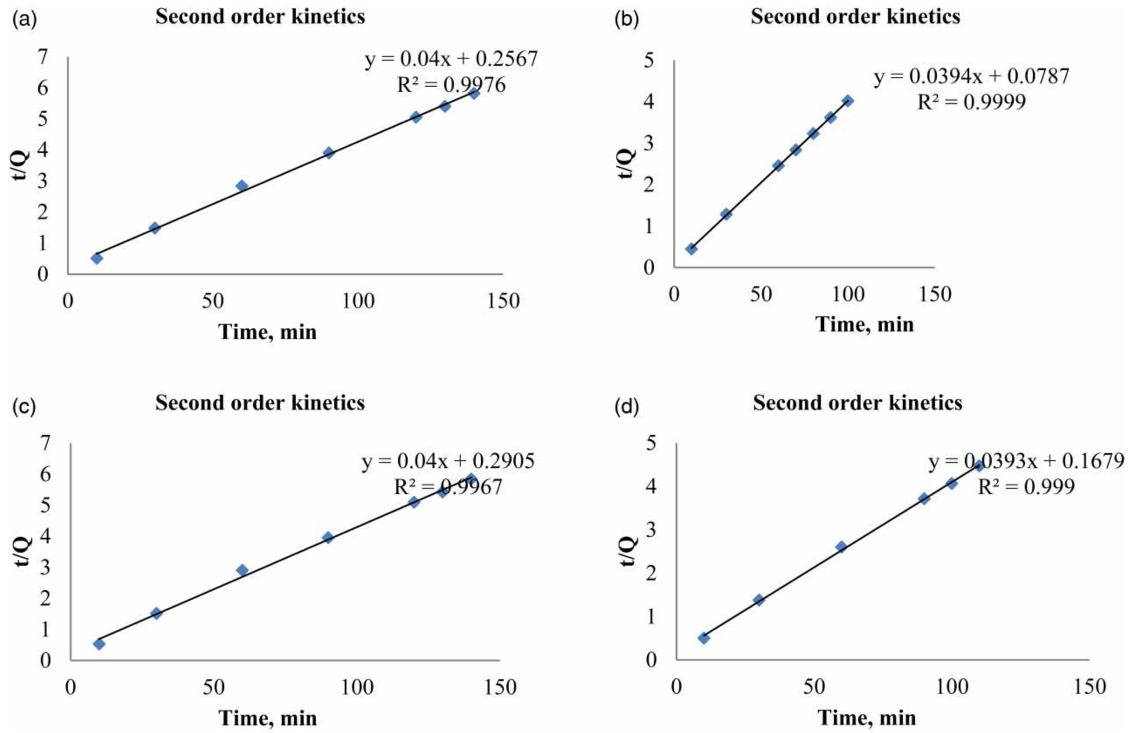

Figure 13 | (a)–(d) Second-order adsorption kinetics of nitrates, nitrites, phosphates and ammonia.

COMPARISON WITH OTHER ADSORBENTS

The adsorption capacity of various adsorbents that have already been used for the removal of nitrates and phosphates has been compared. According to Table 12, none of the researchers used the composite adsorbent to remove nitrates and phosphates. In comparison to the adsorbents listed in Table 12, the removal efficiency of fish scale and neem leaves as novel adsorbents in the removal of nitrates and phosphates is significant.

Table 12 | Comparison of absorption capacities of different adsorbents with the present studied adsorbents

Adsorbent	Nitrate (mg/g)	Phosphate (mg/g)	References
Solid waste residue (SWR) from aluminium sulphate factory	0.065	13.15	Berkessa *et al.* (2019)
Clinoptilolite-Supported Iron Hydroxide Nanoparticle	10.1	9.71	Mikhak *et al.* (2017)
Amine crosslinked magnetic banana bract activated carbon	75.81	91.78	Karthikeyan *et al.* (2020)
Modified commercial activated carbon	21.51	–	Mazarji *et al.* (2017)
Fish scales and neem leaves as novel adsorbent	24.06	23.98	This study

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CONCLUSIONS

This study was carried out to effectively remove four major pollutants, namely nitrates, nitrites, ammonia and phosphates, using waste materials such as fish scales and neem leaves as adsorbents. About 95% to 99% of contaminants could be removed from the considered pollutant concentration range using a combination of fish scales and neem leaves as adsorbents. The percentage removal efficiency for nitrates with the combination of fish scales and neem leaves as novel adsorbent for optimum contact time of 140 min was 96.24%. In contrast, for nitrites, for optimum contact time of 100 min, the value was 99.48%. Similarly, percentage removal efficiency for phosphates and ammonia with the integration of fish scales and neem leaves as novel adsorbent for optimum contact times of 140 and 110 min was 95.92% and 98.38%, respectively, by maintaining the adsorbent dosage as 0.4 g (0.2 g fish scales and 0.2 g neem leaves powder), pH values constant at 6 and temperature value as 303 K. It is evident that when the temperature was varied from 298 to 318 K, the biosorption capacities for the nitrates, nitrites, ammonia and phosphates increased. As a result, thermodynamic studies were done from, which the values of ΔG, ΔH and ΔS were calculated. The negative value of ΔG for all the four pollutants denotes that the adsorption of nitrates, nitrites, ammonia and phosphates on to the fish scales and neem leaves powder as a novel adsorbent is spontaneous and favourable. Based on the enthalpy change (ΔH), which is positive, it can be deduced that the biosorption reaction is endothermic. The Langmuir model is a good fit for the sorption data in the concentration range tested, based on the above investigations and the results of linear regression coefficient (R^2) values. Because the second-order constant K_2 value is much lower than that of the first-order constant K_1, pseudo-second-order kinetics is the ideal model for kinetic data assessments. Furthermore, the values of constant K_2 are observed to rise in the following order: nitrites, ammonia, nitrates, and phosphates, implying that the percentage of pollutants removed increases as the K_2 value increases. Finally, the novel adsorbents, a combination of fish scales and neem leaves, have the potential and success of removing the four significant pollutants, nitrates, nitrites, ammonia, and phosphates, from synthetic aqueous solutions.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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