In-situ synthesised polyaniline - halloysite nanoclay composite sorbent for effective decontamination of nitrate from aqueous streams

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ABSTRACT
Nitrate ($\text{NO}_3^-$) is one of the most common contaminants of water bodies with harmful effects to aquatic life and human beings. There is a need for development of sorbents for effective removal of $\text{NO}_3^-$ from aqueous streams. The aim of present study was to develop a Polyaniline modified halloysite nanoclay (PAni-HC) composite sorbent for the uptake of $\text{NO}_3^-$ from aqueous medium. Aniline coated on halloysite clay was oxidised in acidic medium at 40°C to synthesise PAni-HC composite in one pot reaction. Successful incorporation of polyaniline (PAni) in the clay matrix was confirmed by different surface characterisation techniques. The as synthesised PAni-HC composite sorbent was tested for $\text{NO}_3^-$ sorption in a batch mode in the initial concentration range of 5–500 mg L$^{-1}$. The analysis of $\text{NO}_3^-$ was performed using ion chromatography in the suppressed conductivity mode. The experimental data were assessed using different kinetic and equilibrium models for understanding the sorption behaviour of the PAni-HC composite. Sorption followed pseudo second order kinetics and intraparticle diffusion model. The maximum Langmuir sorption capacity of PAni-HC composite for $\text{NO}_3^-$ was found to be 27.9 mg g$^{-1}$. The composite sorbent when treated with groundwater samples exhibited quantitative removal (> 90%) of $\text{NO}_3^-$ thus demonstrating the applicability of the sorbent in real situations.

1. Introduction
Nitrate ($\text{NO}_3^-$) is one of the vital nutrients for the growth of plants [1]. It is generally supplied in form of fertilisers to increase the crop production. Excessive use of fertilisers attributes high concentration of $\text{NO}_3^-$ in ground and surface water bodies [2–4]. In addition, the disposal of untreated industrial and municipal wastes, landfill leachates, leakage from septic systems etc. contributes to the $\text{NO}_3^-$ pollution in environment [5–7]. It is well-known that in many rural areas throughout the world, groundwater is the only source of drinking water. Consuming water with high concentration of $\text{NO}_3^-$ could lead to...
multiple health hazards in human (stomach cancer in adults and methemoglobinemia or blue baby syndrome in infants) and in livestock [8]. Excess NO$_3^-$ concentrations in different water bodies stimulate the growth of marine plants and algae (known as eutrophication), which in turn is dangerous for the aquatic life and degrades the water quality. Drinking these waters imperils the health of humans and animals [9–14]. In view of the harmful effects of NO$_3^-$, WHO has recommended 50 mg L$^{-1}$ as its safe limit in drinking water [15].

The common water treatment methods for detoxification of NO$_3^-$ include membrane-based separation techniques (reverse osmosis and electrodialysis), chemical/biological denitrification processes, ion exchange, and adsorption processes etc [16–27]. Among all, adsorption being simple and convenient has been considered as the most attractive method [28,29]. Various natural, biodegradable low-cost sorbents or industrial wates have been evaluated for NO$_3^-$ detoxification in terms of economic considerations of the entire process [30–41]. The efficiency or the selectivity of the sorbent can be increased by different physical/chemical surface treatments or by synthesising the composite sorbents by employing any analyte-specific chelating group in the sorbent matrix [42]. The surface treatment methods involve thermal processing, protonation by acid treatment, grafting of different functional groups, surface impregnation of metal oxide and metals, use of organic modifiers, etc. Thermal treatments improve the sorption performance by increasing the porosity and surface area of the sorbent, leading to better access to the functional groups responsible for the analyte uptake. In case of chemical treatments, the enhanced sorption of the analyte is mainly attributed to increase in the number of surface functional groups having higher affinity for analyte or increase in surface charge. In case of composite sorbents, two or more functional materials are combined in such a manner that the synergism improves the sorption capacity of the composite or the selectivity towards the analyte.

For the present studies, a halloysite clay and a polymer – Polyaniline (PAni) has been chosen to synthesise the composite sorbent. Clays are naturally occurring layered aluminosilicates with tetrahedral or octahedral sheet-like arrangement. Halloysite is clay form composed of 1:1 layered sheets with a structural composition Al$_2$Si$_2$O$_5$(OH)$_x$2H$_2$O [43–45], which is very much similar to kaolinite. The active sites available on the surface or in the interlayer spaces of halloysite are instrumental in the removal of ions from the solutions. The different mechanisms involved in the sorption can be ion exchange, coordination, surface complexation, Van der Waals interactions or hydrophobic bonding. The halloysite clays could be useful for environmental clean-up due to the high surface area, structural stability, low cost, easy availability, and sorption properties [46–49]. For the present studies, this clay has been used as a base matrix for the synthesis of composite sorbent.

PAni on the other hand, is one of the well-studied conducting polymers owing to environmental stability, simple method of synthesis, and low cost [50]. In the emeraldine salt form, PAni behaves as an anion exchanger due to the electrostatic interaction between the anions in aqueous medium and positively charged PAni backbone [51–53]. However, the fine structure of PAni makes the phase separation difficult, when employed as an anion exchanger in aqueous medium. Application of composite sorbent could be a solution to this problem. In this view, a composite sorbent was synthesised by using halloysite clay and PAni in a one pot synthesis in the present studies. The physicochemical characterisation of the composite sorbent was carried out using the instrumental techniques such as Fourier transform infrared (FTIR) spectroscopy, X-ray fluorescence (XRF),
Scanning electron microscopy (SEM), X-ray diffraction analysis (XRD) and surface area measurement. The as synthesised sorbent was then used for sorption of \( \text{NO}_3^- \) from aqueous solutions in batch mode under different experimental conditions. For better understanding of the sorption process, the experimental data were correlated to theoretical kinetic and equilibrium models. The composite sorbent was further tested with the groundwater samples for nitrate removal in view of real applications.

2. Experimental

2.1. Materials

All commercially available analytical reagent grade chemicals were used for the present studies. Hydrochloric acid (HCl), ammonium persulphate(APS), aniline, acetonitrile and sodium nitrate (99.99\% purity) were obtained from Sigma Aldrich. Aniline was purified by distillation prior to its use in the synthesis [54]. Appropriate amount of \( \text{NaNO}_3 \) was dissolved in deionised (DI) water to prepare a stock standard solution of \( \text{NO}_3^- \) (1 g L\(^{-1}\)). The working standard solutions (5–500 mg L\(^{-1}\)) were made by appropriate dilutions using stock standard solution. The DI water with resistivity 18.2 MΩ.cm have been used for all the experiments.

2.2. Synthesis of PAni-HC composite

The synthesis of PAni-HC composite was performed in the following manner. 10 g of halloysite clay was mixed to a solution containing 2 mL aniline in 250 mL of 1 M HCl. In another container, 6 g of APS (oxidant) was taken in 100 mL of 1 M HCl. Both containers were maintained at 4ºC for 2 h. APS was then added with continuous stirring to the clay-aniline mixture and the resultant mixture was maintained undisturbed overnight. Next day, the composite product was separated from supernatant by centrifugation performed at 7000 rotations per minute (rpm) for 20 min. It was then washed with DI water several times and the final washing was given with acetonitrile to remove low-molecular-weight oligomers and other soluble impurities followed by air drying.

2.3. Characterisation of the PAni-HC composite

Characterisation of PAni-HC composite was carried out using FTIR, XRF, SEM, XRD and Surface area analyses. The surface functional groups available in the bare clay and PAni-HC composite were recorded in the range of 500 to 4000 cm\(^{-1}\) using IR Affinity-1 FTIR spectrometer. XRF analysis was performed at room temperature using a Jordan Valley EX-3600 M spectrometer under vacuum to determine the major elemental composition of the sorbents. The optimised conditions for the analysis are: emission current = 2000 \( \mu \)A, applied voltage = 5 kV, Rh-secondary target and counting time = 50 s. The change in the surface morphology of bare clay after functionalization with PAni was investigated by SEM analysis using VEGA MV 2300 T Scanning Electron Microscope. X-ray powder diffraction (XRD) patterns were recorded at room temperature using Cu K\( \alpha \) (0.15406 nm) radiation and silicon as external standard in a 10º-70º range (26) with a step of 0.02º.
Surface area measurements were performed by V-Sorb2800 S surface area analyser, using a BET method of N₂ absorption by heating the sample at 130°C for 3 h.

### 2.4. Batch sorption studies and NO₃⁻ analysis

Sorption behaviour of PANi-HC composite for NO₃⁻ (5–500 mg L⁻¹) was studied in batch mode at room temperature and at pH 6.0. The NO₃⁻ solutions (10 mL) with 0.1 g of sorbent were agitated for a fixed time in a rotary shaker followed by centrifugation at 15,000 rpm to separate the two phases. The concentration of NO₃⁻ in the residual solutions was determined by ion chromatography (IC) in a suppressed conductivity mode using Dionex ICS-5000 instrument. IC analysis comprised IonPac AS11-HC Dionex (4 mm X 250 mm) analytical column (connected to IonPac AG11-HC Dionex (4 mm X 20 mm) guard column) maintained at 30°C as the stationary phase and 25 mM NaOH at the flowrate of 0.5 mL min⁻¹ as the eluent for the separation of NO₃⁻ ions. The background conductivity due to the eluent was reduced using a suppressor ASRS 400 (4 mm) operating at the current of 31 mA and the signal is detected by conductivity detector followed by its processing using Chromeleon v2.0 data analysis software. The sorption kinetics for NO₃⁻ was investigated up to a period of 420 min. For these studies, 50 mL of 100 mg L⁻¹ NO₃⁻ solution with 0.5 g of PANi-HC composite was agitated continuously in rotary shaker. After the fixed time intervals, supernatant solution was analysed for residual NO₃⁻ concentration. The application of the PANi-HC composite sorbent for decontamination of NO₃⁻ in real samples has been tested. Three groundwater samples (before and after spiking with NO₃⁻ ions) were treated with a 0.1 g of PANi-HC composite till it reaches equilibrium and the residual NO₃⁻ concentration was investigated. All the experiments were performed in triplicates.

Amount of NO₃⁻ sorbed (qₜ in mg g⁻¹) can be given as follows:

\[ qₜ = \frac{(C₀ - Cₜ)}{M} \times V \]  \hspace{1cm} (1)

Where, \( C₀ \) is the initial concentration of NO₃⁻ ions and \( Cₜ \) is its concentration after time \( t \) (mg L⁻¹), \( V \) is the volume of solution (L) and \( M \) is the mass of the sorbent (g).

The % of sorption for NO₃⁻ can be determined by following equation

\[ \% \text{ Sorption} = \frac{(C₀ - Cₜ)}{C₀} \times 100 \]  \hspace{1cm} (2)

### 2.5. Assessment of experimental data with theoretical models

For understanding the interaction between the analyte and the composite sorbent, the sorption data were assessed with different kinetic and equilibrium models. The findings from this correlation could be useful for designing and optimising the nitrate sorption process at higher scale.
2.5.1. Sorption kinetics
The pseudo first order, pseudo second order and intra particle diffusion kinetic models were applied to the sorption data to get an insight to the potential rate-controlling steps and the sorption mechanism [55,56].

The linearised first order kinetic models can be given as follows

\[ \log(q_e - q) = \log q_e - \frac{(K_1 t)}{2.303} \]  

(3)

where, \( q_e (\text{mg g}^{-1}) \) and \( q (\text{mg g}^{-1}) \) are the amount of NO\textsubscript{3}\textsuperscript{−} ions taken up by the sorbent at equilibrium and at time \( t \) respectively. \( K_1 (\text{min}^{-1}) \) is the first order rate constant, which can be determined from the plot of \( \log(q_e - q) \text{ Vs } t \).

The linearised second order kinetic model can be expressed as follows.

\[ \frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \]  

(4)

where, \( K_2 (\text{g mg}^{-1} \text{ min}^{-1}) \) is the second order rate constant.

The applicability of the pseudo second order kinetics to the experimental data can be checked by the plot of \( t/q \text{ Vs } t \). The values of \( K_2 \) and \( q_e \) can be derived from the intercept and slope of the plot, respectively.

The sorption of a liquid sorbate on the surface of solid sorbent is a stepwise process involving the transport of analyte molecules from the liquid phase to the surface of the sorbent followed by their diffusion inside the solid matrix and finally the sorption at the site. The second stage of diffusion into the interior of sorbent is generally a slow process. The evaluation of intraparticle diffusion as a rate determining step for sorption process can be done by a mathematical model [57], which is given as follows.

\[ q = K_{id} t^{0.5} \]  

(5)

where \( K_{id} \) is the intraparticle diffusion rate constant. The value of \( K_{id} \) can be obtained from slope of a plot of \( q \text{ vs. } t^{0.5} \).

2.5.2. Sorption equilibrium isotherms
The sorption equilibrium data have been correlated with Freundlich and Langmuir isotherms [58,59] to get an idea about the NO\textsubscript{3}\textsuperscript{−} uptake capacity and affinity between the NO\textsubscript{3}\textsuperscript{−} ions and PANi-HC composite sorbent.

The Freundlich isotherm based on sorption on heterogeneous surfaces is expressed by the following equation.

\[ q_e = KF(Ce)^{1/n} \]  

(6)

Where, \( q_e (\text{mg g}^{-1}) \) is the amount of NO\textsubscript{3}\textsuperscript{−} ions taken up by the sorbent at equilibrium, \( C_e (\text{mg L}^{-1}) \) is the residual equilibrium NO\textsubscript{3}\textsuperscript{−} ions concentration, \( K_F \) and \( n \) are constant related to the sorption capacity and sorption intensity, respectively.

Langmuir equation is based on monolayer coverage of sorbate on the structurally homogeneous sorbent (with identical and energetically equivalent sorption sites) with a fixed sorption capacity. The equation for Langmuir isotherm is given as
3. Results and discussion

3.1. Synthesis and characterisation of PANi-HC composite

PAni-HC composite sorbent was developed by in-situ synthesis of PANi in a one pot reaction on the halloysite clay support matrix through oxidative chemical polymerisation technique [61–64] using aniline monomer and APS oxidant in acidic medium. The as synthesised PAni-HC composite has positive charge on its polymeric backbone along with Cl⁻ counter ions for charge neutralisation. The successful incorporation of PANi on the clay matrix has been analysed by different physico-chemical characterisation techniques namely FTIR, XRF, SEM, XRD and surface area measurements. FTIR spectrum of native clay and PAni-HC composite in the range of 500–4500 cm⁻¹ is given in Figure 1a. The peak at 3622 cm⁻¹ is attributed to the stretching vibrations of Al-O-H coordination. The bands at 3695 cm⁻¹ and 1643 cm⁻¹ are corresponding to the stretching and bending vibrations of H-O-H groups of surface adsorbed water molecules of clay and PANi. The sharp peak at 1004 cm⁻¹ and 794 cm⁻¹ are due to the stretching vibration modes of Si-O-Si. The peak at 908 cm⁻¹ corresponds to the vibrations of Al-O-Al bond. Thus, the bands present in the region of 1200–400 cm⁻¹ are mainly due to the stretching and bending vibrations of the aluminosilicate framework. In case of PAni-HC composite, the peaks at 1463 and 1552 cm⁻¹ corresponds to the benzenoid and quinoid ring of PANi, respectively. The peaks at 1296(C-N stretching), 1242 (C = N stretching) and 1116 cm⁻¹ (aromatic C-N-C stretching) can be correlated with the oxidation or protonation states in PANi [65]. The Si-O-Si frequency of the clay matrix (1004 cm⁻¹) is shifted to 999 cm⁻¹ in the composite, which can be attributed to the Coulombic interaction between the partial negatively charged clay layers and positive nitrogen of the intercalated PANi.

The XRF spectra are given in Figure 1b. The signature peaks of various elements with respect to Kα energy values indicate the presence of Al and Si in both bare clay and composite sorbent. XRD analysis showed that the clay has a structure of Al₂Si₂O₅(OH)₄ as observed from PCPDFWIN [PDF number 090453] (Spectra not shown here). Thus, the XRF results corroborate with those obtained from XRD. Surface area of bare clay and PAni-HC composite was found to be 51 and 33 m² g⁻¹ respectively. The reduction in the surface area for composite as compared to bare clay is due to the formation of the PANi in the interlayers of the clay material. SEM images of bare clay and PAni-HC composite are shown in Figure 1c-d. The surface coverage of the clay with PANi is clearly seen with the bright particles over the clay surface.

\[ q_e = \frac{Q^0 b C_e}{1 + b C_e} \] (7)

Where, \( Q^0 \) (mg g⁻¹) is the mass of NO₃⁻ ions required to completely cover the unit mass of the sorbent. It is also known as the limiting sorption capacity of the sorbent. The constant \( 'b' \) (L mg⁻¹) is related to the energy of sorption.

An important parameter of Langmuir isotherm, known as equilibrium parameter or separation factor, \( R_L \) is given by the following equation.

\[ R_L = 1/(1 + b C_0) \] (8)

\( R_L \) is a dimensionless factor and indicative of the type of isotherm. The value of \( R_L \) should be 0 < \( R_L < 1 \) for favourable sorption [60].
3.2. Nitrate sorption studies

3.2.1. Influence of contact time on nitrate uptake

Equilibrium contact time is a crucial parameter in determining the efficiency of any sorption system. Herein, the influence of contact time on NO$_3^-$ (100 mg L$^{-1}$ of initial concentration) sorption using PAni-HC composite sorbent was studied for a period up to 420 min. The corresponding observation has been plotted in Figure 2(a). It is clear from the figure that, more than 90% of the NO$_3^-$ uptake was accomplished within the first 10 min of contact followed by the gradual uptake and the equilibrium has been attained in 120 min. The high uptake rate in the initial stages of sorption can be attributed to the large availability of vacant binding sites on the sorbent surface for interacting with the NO$_3^-$ ions. The following gradual uptake is resulting from comparatively slow mass transfer of NO$_3^-$ to the interior sites of the sorbent. The 3 h contact time was fixed for

Figure 1. Characterisation of the PAni-HC composite sorbent using different techniques: a) FTIR analysis; b) XRF analysis; and SEM images of c) Bare Halloysite clay and d) PAni-HC composite sorbent.
further experiments to make sure the attainment of equilibrium at higher initial concentration of NO$_3^-$.

The kinetic data were tested with pseudo first order, pseudo second order and intraparticle diffusion kinetic models (Figure 2b-d). The best fit model was selected on the basis of matching the theoretical and experimental values of uptake of nitrate ion and adjusted determination coefficients ($R^2_{adj}$). Table 1 shows the sorption kinetic rate constants obtained from correlating the experimental data with these models. The value of $R^2_{adj} = 1$ clearly indicates the suitability of pseudo second order kinetic model to the experimental data in comparison with pseudo first order model ($R^2_{adj} = 0.85$). The pseudo-

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**Table 1.** Sorption rate constants associated with uptake of NO$_3^-$ using PAni-HC composite sorbent.

| Kinetic model           | Parameter | Values  |
|-------------------------|-----------|---------|
| First order kinetics    | $K_1$(min$^{-1}$) | 0.053   |
|                         | $q_{e,cal}$(mg g$^{-1}$) | 0.22    |
|                         | $R^2_{adj}$ | 0.85    |
| Second order kinetics   | $K_2$     | 1.03    |
|                         | $q_{e,cal}$(mg g$^{-1}$) | 4.21    |
|                         | $R^2_{adj}$ | 1.0     |
| Intraparticle Diffusion | $K_{id}$ (mg g$^{-1}$ min$^{-1}$) | 0.94    |
|                         | $R^2_{adj}$ | 0.97    |

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second order kinetic model assumes that the rate-limiting step may be chemisorption, which involves the valency forces through sharing or exchange of e⁻s between the sorbent and sorbate [66,67]. For the present studies, pseudo second order kinetic model provides the best correlation with the experimental data indicating the involvement of chemisorption in the uptake of NO₃⁻ using the composite sorbent.

The migration of the solute towards the sorption sites in the solid – liquid system can take place by film diffusion and/or particle diffusion. Herein, the role of film diffusion in the migration of NO₃⁻ ions was minimised by shaking the experimental solutions at 200 rpm and thus reducing the boundary layer resistance. Therefore, the film diffusion could no more control the rate of the sorption. As discussed above the sorption of nitrate ions could be split into three different stages. It includes the first rapid uptake of NO₃⁻ ions owing to the large availability of vacant binding sites on the surface of sorbent followed by gradual uptake due to the migration of the ions to the interior sorption sites and finally the attainment of equilibrium. Application of intraparticle diffusion model to the experimental data where the gradual uptake of NO₃⁻ is taking place, has been shown in the Figure 2(d). The agreement of data to the respective model with \( R^2_{adj} = 0.97 \) reveals that the sorbate migration follows the intraparticle diffusion. However, the plot does not pass through the origin, indicating that though intraparticle diffusion is involved, influence of film diffusion cannot be totally ignored.

### 3.2.2. Effect of initial nitrate concentration and sorption isotherms

The influence of initial concentration on NO₃⁻ uptake has been studied for PANi-HC composite (Figure 3a). The uptake of NO₃⁻ increases with increasing initial concentration, which could be resulted from the concentration-dependent mass transfer of NO₃⁻ ions. The PANi-HC composite showed higher uptake of nitrate as compared to the bare clay sorbent. Enhanced sorption of NO₃⁻ ions in the case of composite sorbent could be attributed to the presence PANi. The sorption mechanism has been discussed in detail in the following section. The non-linear sorption equilibrium isotherms for the present data and the corresponding sorption constants are given in Figure 3(b) and Table 2, respectively. For bare clay sorbent, Langmuir isotherm fits better than Freundlich indicating the monolayer sorption of nitrate with maximum sorption capacity \( Q^0 \) 3.3 mg g⁻¹. ForPAni-HC composite, the value of \( Q^0 \) determined from the Langmuir isotherm was 27.9 mg g⁻¹. The surface modification of halloysite with PANi clearly exhibited a 9-fold increase in the uptake capacity of NO₃⁻.The value of Freundlich constant, \('n'\) lies between 0 and 1, revealing the sorption is favourable in the present case. The value of \( R^2 \) for clay and for PANi-HC composite within the studied concentration range (5–500 mg L⁻¹) was found to be in the range of 0.95–0.17 and 0.98–0.37, respectively. This also supports the earlier finding of favourable sorption in case of both the sorbents.

### 3.3. Mechanism of nitrate sorption by the PANi-HC composite

For the illustration of NO₃⁻ sorption mechanism using PANi-HC composite, the individual roles of halloysite clay and PANi in the composite need to be understood. Halloysite clay can take up both anions as well as cations via ion exchange, coordination, surface complexation, Van der Waals interactions or hydrophobic bonding. However, sorption of anions is less as compared to cations in halloysites as the isomorphous structural substitution leads to the overall negative charge on the surface and is balanced by trapping cations. It is
reported that the surface complexation at the crystal edges in the halloysite clay is the mechanism mainly responsible for the sorption of anions [68]. In the present case, the same could be expected. Upon incorporation of PANi in the halloysite matrix, about 9-fold increase in the $\text{NO}_3^-$ sorption capacity was observed. The equilibrium and kinetic data, as discussed in previous sections, reveal the chemical nature of $\text{NO}_3^-$ sorption by the PANi-

**Figure 3.** Sorption equilibrium of $\text{NO}_3^-$ using PANi-HC composite sorbent: a) Influence of initial concentration of $\text{NO}_3^-$ and b) application of theoretical equilibrium isotherms to experimental data.
HC composite and its strong dependence on the amounts of both the sorbate and sorbent. The present results show that the interaction of $\text{NO}_3^-$ with the PAni-HC composite occurs via the ion exchange phenomenon. The weak anion exchange capacity of PAni arises from the ionisable chloride present in it. Chloride ions get attached to the functional amine groups of PAni, during synthesis in HCl medium. During sorption studies, $\text{NO}_3^-$ was quantitatively taken up by the composite sorbent in exchange of $\text{Cl}^-$ ions. The stoichiometric ion exchange process was confirmed by the amount of chloride in the effluent, as tested by ion chromatography analysis. This is in accordance with the existing literature on the higher selectivity of anion exchangers for nitrate over chloride ions [69].

A schematic illustrating the synthesis of PAni-HC composite and uptake of $\text{NO}_3^-$ over the composite sorbent is given in Figure 4. From all the above discussion, the entire process of synthesising the composite and the uptake of $\text{NO}_3^-$ ions can be described in the following steps:

1. Diffusion of anilinium cations in the interlayer spaces of the halloysite clay sheets and sorption due to electrostatic attraction.
2. Oxidative chemical polymerisation of anilinium ions in the halloysite matrix in acidic medium to form PAni-clay composite.
3. Treatment of $\text{NO}_3^-$ ions with PAni-HC composite sorbent – leads to ion exchange of $\text{NO}_3^-$ ions with $\text{Cl}^-$ counterions from composite.

### 3.4. Application of the PAni-Clay composite for nitrate decontamination

The development of any sorbent remains incomplete unless its performance is tested for real samples. The present work was aimed at decontamination of nitrate from groundwater samples using the as synthesised PAni-HC composite sorbent. Three groundwater samples (10 mL each) were treated (before and after spiking with 50 and 75 mg L$^{-1}$ $\text{NO}_3^-$) with 0.1 g of PAni-HC composite and the concentration of $\text{NO}_3^-$ in the samples was determined. The pH of all the three samples was in the range of 6.5–7.0. It was observed that all the three samples contained $<2$ mg L$^{-1}$ $\text{NO}_3^-$ initially, which after treatment with the composite sorbent reduced to $<0.2$ mg L$^{-1}$. The experimental observations are given in Table S1. It is clear from the table that $>90\%$ of $\text{NO}_3^-$ has been removed from all the three samples. The relative standard deviation ($\text{RSD}$) of the analysis was found to be $<5\%$. These samples when spiked with 50 and 75 mg L$^{-1}$ of $\text{NO}_3^-$ showed that the level of $\text{NO}_3^-$ was reduced well below the specified limit for drinking water. The experiments illustrated the applicability of the composite sorbent in real situations.
3.5. Comparison of sorption performance of the PAni-HC composite with other sorbents

Sorption studies of nitrate have been carried out by various native and surface modified natural materials till date. A tabular representation of the values towards the sorption capacity for NO$_3^-$ of these sorbents at the respective set of experimental conditions has been given in Table S2 [30,32,34–37,40–41,70–81]. Though the experimental conditions are not identical in all the cases, the comparison of sorption capacity of different sorbents provides information regarding the performance of the individual material. The sorption capacity of PAni-HC composite for nitrate was found to comparable with many other reported sorbents.

4. Conclusions

The synthesis, characterisation and sorption behaviour of PAni-HC composite sorbent has been reported herein. The structural characterisation of the composite sorbent confirms the signature of polyaniline within the halloysite clay matrix. The sorption for the present system follows second order kinetics with intraparticle diffusion playing an important role in the sorbate migration towards the sorbent surface. PAni-HC composite exhibited a multi-fold-enhanced sorption performance as compared to bare clay sorbent with Langmuir sorption
capacity of 27.9 mg g\(^{-1}\). The ion exchange of NO\(_3^-\) with Cl\(^-\) counterions from the PANi structure is the dominating mechanism for NO\(_3^-\) removal. The present composite material shows the potential for further application for NO\(_3^-\) removal from aqueous systems.

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**Disclosure statement**

No potential conflict of interest was reported by the authors.

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