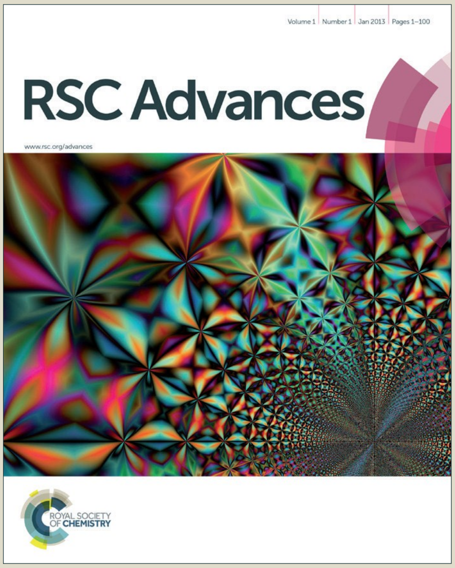
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Kinetic and equilibrium modeling for removal of nitrate from aqueous solutions and drinking water by a potential adsorbent, hydrous bismuth oxide

Prabhat Kumar Singh[a], Sushmita Banerjee[b], Arun Lal Srivastava[c], Yogesh Chandra Sharma[c*]

[a]Department of Civil Engineering, Indian Institute of Technology (BHU) Varanasi, Varanasi 221005, India.

[b]Department of Chemistry, University of Allahabad, Allahabad 211002, India.

[c]Department of Chemistry, Indian Institute of Technology (BHU) Varanasi, Varanasi 221005, India.

*Corresponding author

E Mail ysharma.apc@iitbhu.ac.in; Tel No +91 542 6702865; Fax +91 5422368428

Manuscript submitted for publication in:

RSC Advances

Kinetic and equilibrium modeling for removal of nitrate from aqueous solutions and drinking water by a potential adsorbent, hydrous bismuth oxide

Prabhat Kumar Singh[a], Sushmita Banerjee[b], Arun Lal Srivastava[c], Yogesh Chandra Sharma[c*]

[a]Department of Civil Engineering, Indian Institute of Technology (BHU) Varanasi, Varanasi 221005, India.

[b]Department of Chemistry, University of Allahabad, Allahabad 211002, India.

[c]Department of Chemistry, Indian Institute of Technology (BHU) Varanasi, Varanasi 221005, India.

*Corresponding author

E Mail ysharma.apc@iitbhu.ac.in; Tel No +91 542 6702865; Fax +91 5422368428

Abstract

Kinetic, equilibrium modeling and adsorption characteristics of Hydrous bismuth oxides (HBOs) have been investigated for the removal of nitrate from aqueous solutions. The three HBO samples, designated as HBO_1, HBO_2 and HBO_3 were synthesized by controlled precipitation method. Among three HBO samples, HBO_3 accounts for maximum nitrate uptake of 0.22 mgN/g with an initial nitrate concentration of 14 mgN/L therefore same was selected for the detailed studies. HBO_3 was characterized by various instrumentation techniques which includes X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy and energy dispersive spectrometry. The adsorption characteristics and process variables were investigated by examining different parameters such as pH, contact time, initial nitrate concentration and temperature. Solution pH remarkably influences the nitrate sorption process as the sorption capacity found to be increases from 0.056 to 0.22 mgN/g with the increase of pH value from 2.0-7.0. The sorption capacity also found to increase with increasing concentration, temperature while presence of competing anions such as Cl^-, HCO_3^- and SO_4^{2-} severely impedes nitrate sorption capacity. The sorption kinetic data found to be consistent with pseudo-first-order kinetic model. The equilibrium data agrees well with Freundlich model and the highest monolayer adsorption capacity of HBO_3 for removal of nitrate ions was found to be 0.97 mgN/g at 313 K. The investigation of thermodynamic parameters indicated spontaneous and endothermic nature of sorption process. In a nutshell HBO_3 shows great potential for removal of nitrate ions from aqueous solution as well as drinking water.

***Key words**:* Hydrous bismuth oxide, Nitrate removal, Kinetics, Equilibrium modeling, Thermodynamics.

1. Introduction

Majority of global population depends on ground water for drinking purpose. Nitrate concentration in ground and surface waters is increasing in many parts of the world including India[1].In general, groundwater has been contaminated by anthropogenic and geogenic inorganic substances such as nitrate, fluoride, arsenic etc[2]. Global use of fertilizers for intensive agriculture has increased the amount of reactive nitrogen in terrestrial and aquatic ecosystems[3-4]. High nitrate contaminated water consumption is reported to cause various health related problems such as methemoglobinemia, stomach cancer, increased infant mortality, central nervous system birth defects, non-Hodgkin's lymphoma, initiation of kidney diseases, oral cancer, cancer of colon, rectum and other gastrointestinal cancers and Alzheimer's disease[1,5]. Besides nitrogenous fertilizers, animal wastes, municipal wastes, landfills, septic tanks and soil organic matters are major sources of nitrate contamination of groundwater.[6] The current maximum allowable concentration of nitrate in drinking water as prescribed by Bureau of Indian Standards (BIS) [7] is

45 mgNO$_3^-$/L and World Health Organization[8] has suggested a guidelines value of 50 mgNO$_3^-$/L. The common methods of nitrate removal from water are reverse osmosis, ion-exchange, catalytic reduction, biological de-nitrification and adsorption[1, 9-11]. Adsorption is considered a better option for water treatment at small scale due to its ease of operation, convenience and simplicity of design.[12-16] It can remove different types of organic and inorganic pollutants from the water or wastewater[15]. Bhatnagar and Sillanpaa[15] have reported different adsorbents for the removal of nitrate from water and wastewater on the basis of their origin. Several researchers have reported treatment of water contaminated with fluoride and arsenic[17-22,23] using inorganic materials as adsorbents. Hydrated alumina[23,24], and nano-alumina[1,2324-24,25] have been efficiently reported for removal of nitrate from water.

Fristche and Singh and Ghosh[25-2626-27] have found that polymeric forms of hydrous bismuth oxides (HBOs) are efficient for the removal of nitrate from water. Singh et al.[1]summarized the methods of preparation and properties of hydrous bismuth oxides (HBOs) for nitrate removal from aqueous solutions. They proposed that probably presence of greater amount of hydroxide in the reaction would have been responsible for polymerization of monomeric hydrous bismuth oxide and such polymerized HBOs presented appreciable removal of nitrate from water. Three HBO powders, designated as HBO$_1$, HBO$_2$ and HBO$_3$ (prepared using 0.1M Bi_2O_3 solution in 2N HCl with increasing volumetric proportions of 1:1, 1:2 and 1:3 of 2N NaOH, washed and dried) and tested for nitrate sorption potentials at 14 mgN/L initial concentration and shows reasonable sorption capacity of 0.16, 0.19, 0.22 mgN/L respectively. Besides the application of HBOs as an adsorbent for wastewater remediation it is also necessary to assess its possible toxic effects in aquatic and soil environment. Although it has been accounted that bismuth compounds have low solubility and are not considered to be toxic.[28] There is still limited information report on bismuth toxicity.

However in order to ensure the as-synthesized materials were toxic free and harmless to environment we therefore conduct a brief study to observe the effect of HBO on germination capacity of *Cicer arietinum* seeds. The experiment was performed by soaking 5.0 g of seeds of *Cicer arietinum* (seeds were treated with 10% sodium hypochlorite solution to maintain surface sterility prior to its use during experiment) in two different beakers of volume 250 mL, in first beaker 2.5 g of HBO was added in 100 mL of distilled water while second beaker contains only 100 mL of distilled water. The beakers were then kept for overnight so that water imbibes into the seeds appropriately. Next day well imbibe swollen seeds of *Cicer arietinum* from both beakers were collected and wrap in two different moist muslin cloths which triggered seed sprouting. The cloth was checked frequently so that it not gets dried and affects sprouting process. In fourth day seeds were finally taken out from the wrapped cloth and both types of seeds were compared in terms of seed size, sprout length and seed coat color. It has been observed that apparently no significant differences was tracked between the water imbibe and HBO + water imbibe seedlings. In both case seeds were developed with healthy white sprout of length in range of 2.0 to 2.7 cm, no change in color have been observed for seed coat and the germinated seeds seems to be capable enough to grow into healthy plants. This observation is somewhat helpful in addressing the environmental toxicological aspect however this experiment is not the ultimate finding which guaranteed non toxic nature of HBO. Similar experiments were also carried out by Ma et al.[29], Tripathi et al.[30] and Zhai et al.[31] to investigate the toxicity of rare earth oxide nanoparticles, carbon nanotubes and Pr $(OH)_3$ nanostructures respectively by employing higher plant species.

In present study the potential of HBO_3 as an adsorbent material for the removal of nitrate ion from aqueous solutions has been undertaken. The sorption capacity of the material found to be increased with increasing initial concentration of nitrate and water temperature. Out of the three HBOs, $HBO_3$was found to be the best for the removal of nitrate; it was selected for detailed studies.

Characterization of HBO_3 was carried out by X-ray diffraction analysis, Fourier transform infrared spectrum analysis, scanning electron microscopy and energy dispersive spectrometry. Kinetic and equilibrium studies for the removal of nitrate from aqueous solutions were conducted. The thermodynamic parameters such as change in Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were also determined for the system undertaken.

2. Materials and methods

2.1 Synthesis of adsorbent

Bismuth trioxide powder of AR grade was used to synthesize the HBOs used for the removal of nitrate from aqueous solutions and the method reported by Fristche[26] for synthesis of 'yellow bismuth hydroxide' was adopted for synthesis of HBO_3.For HBO_3, 100mL of 0.1 M Bi_2O_3 (in 2N HCl) was mixed with 300mL of 2N NaOH, and the reaction was carried out for 1 h with thorough mixing. A yellow precipitate was obtained which was filtered and liberally washed with distilled water to remove the excess hydroxide and chloride ions. The precipitate was dried in oven at 100±3°C for 24h and a powdered HBO_3 was obtained which was subsequently used in the experiments.

2.2Instrumentation

Ion Selective Electrode (ISE) (HANNA HI 4222, Hanna Equipments Pvt. Ltd, Navi Mumbai, India) as per APHA[32] was used to determine residual concentration of nitrate in the solutions. pH of the solutions was also determined by the same instrument. For determination of nitrate in aqueous solutions, 2-3 mL of ISA (Ionic Strength Adjustment, HI 4013-00) solution was added in

50 mL of sample in a beaker of 100 mL. The content was stirred with a magnetic stirrer for 1 min. Using the appropriate ISE, the electrode tip was immersed in the sample and reading was recorded when the value became almost stable.

2.3 Batch experiments for nitrate adsorption

Batch experiments were conducted to study the removal of nitrate onto HBO_3powder. Potassium nitrate (AR grade) was used to prepare all standard nitrate solutions for the work. Required amount of the adsorbent was added to the solution taken in 100mL stoppered bottles, which were placed in a thermostat shaking water bath. The contents were continuously stirred at constant temperature and after every 5 minutes of interval the flasks taken out from the water bath and filtered using Whatman 42 filter paper. The filtrates were then analyzed for residual concentration of nitrate. The process repeated until equilibrium established. After optimization of contact time other parameters such as effect of pH, temperature, interfering anions were investigated at already optimized contact time period. All experiments were carried out in triplicates and the average of the three observations was taken and reported.

The adsorption capacity, q_e (mgN/g) of HBO_3 was estimated using the following expression:

$$q_e = \frac{C_i - C}{m} \qquad (1)$$

where, C_i,initial concentration of nitrate (mgN/L), C, residual concentration of nitrate in solution after adsorption (mgN/L), and m, mass (g) of HBO_3per liter of solution.

The removal (%) of nitrate was calculated as follows:

$$\text{Removal of nitrate (\%)} = \left(\frac{C_i - C_e}{C_i}\right) \times 100 \qquad (2)$$

where, C_i and C_e are the initial and final concentrations of nitrate(mgN/L).

2.4Kinetic studies

For kinetic studies, 100 mL nitrate solution was mixed with 5g (i.e.@50g/L) of $HBO_3$and was agitated for 5 to 420 min in a temperature-controlled thermostatic water bath shaker. All experiments were conducted for four initial nitrate concentrations: 14, 28, 42 and 56 mgN/L. After pre-selected time interval, the adsorbent was separated from the solution by filtration and the aliquot was analyzed for residual nitrate concentration in the solution.

2.5 Equilibrium studies

Batch experiments for adsorption of nitrate on HBO_3 were conducted at three temperatures (293, 303 and 313 K) for six initial nitrate concentrations solution (14, 28, 42, 56, 70 and 84 mgN/L). 100 mL of nitrate solution of all the six initial concentrations with 50 g/L of adsorbent for three hours of contact time in a temperature-controlled shaking water bath shaker. After three h, samples were filtered and the filtrate was then analyzed for pH and residual concentration of nitrate by ion meter. Thermodynamic parameters and the effect of temperature on nitrate removal by HBO_3 powder were also observed.

2.6Characterization of the adsorbent

Characterization of the adsorbent, HBO_3 powder was carried out by using different instrumentation techniques includes FTIR, XRD, SEM and EDS. pH_{ZPC} of the adsorbent was determined through solid addition method as reported by Sharma et al.[33] FTIR spectrum was collected using FTIR spectrometer (Perkin Elmer spectrum RX1), X-ray diffraction (XRD) patterns of HBO_3 obtained using X-ray diffractometer (Philips 1710, Netherland). Study on surface morphology was carried out by Scanning Electron Microscope (SEM) (Leo, USA, 435 VP). Elemental analysis was conducted through (SEM) (Leo, USA, 435 VP).

2.7 Determination of pH_{ZPC}

For determination of pH_{ZPC}, initial pH of 0.01 M NaCl was adjusted in 4.0 to 12.0 range by 0.1 N HCl or NaOH. 50 mL of 0.01 M NaCl was taken in 250 mL Erylenmeyer flasks and 0.20 g of HBO_3 was added to each solution and flasks were left for 48 h and the final pH of the solutions was measured. A plot was obtained between "pH_{final} vs $pH_{initial}$". The intersection point of this plot (pH_{final} vs $pH_{initial}$) has been defined as pH_{ZPC} for surface of HBO_3.

3. Results and discussion

3.1 Adsorption of nitrate on HBO_3 powder

The three HBO powders, designated as HBO_1, HBO_2 and HBO_3were synthesized by 0.1M Bi_2O_3 solution in 2N HCl with increasing volumetric proportions of 1:1, 1:2 and 1:3 of 2N NaOH. The powdered HBOs were washed repeatedly with distilled water and dried at 103±2ºC) and were examined for the removal of nitrate from its aqueous solutions at initial concentration of 14 mgN/L. HBO_3 showed highest nitrate sorption potential from the aqueous solutions. The sorption capacity increased with increasing initial concentration of nitrate and temperature of the solutions. The pH of water treated with $HBO_3$was found to be ~7.5. It was taken as an indication that hydroxyl ions are not competing with nitrate ions for the active sites available on the surface of HBO_3.

3.2 Characterization of HBO_3 adsorbent

3.2.1 X-ray Diffraction pattern analysis

Fig.1a shows the XRD diffractogram of HBO_3 powder. Presence of prominent peaks clearly indicates about the crystalline characteristics of HBO_3 powder. The presence of strong peaks at 2θ

values of 25^0, 29.36^0, 33.18^0, 43.70^0, 53.54^0, 57.53^0, 62.87^0, 66.61^0 and 72.96^0 with d spacing values of 3.559, 3.215, 3.142, 2.815, 2.229, 1.915, 1.826, 1.732, 1.672 and 1.575 Ǻ respectively is in agreement with JCPDS Card no.73-2062 which represented presence of Bi_2O_3. Similar peaks were also observed by Xiao et al.[34] for Bi_2O_3 powder. The peaks corresponding to $2\theta = 30.23^0$, 32.78^0, 32.85^0 and 56.91^0 with d spacing values of 3.058, 2.844, 2.839 and1.855 Ǻ respectively indicates formation of bismuth hydroxide [$Bi(OH)_3$] (as per the JCPDS Card no. 01-0898).

3.2.2 FTIR analysis

Fig. 1b shows the FTIR spectrum of HBO_3 powder. The major absorption bands are found at 474 cm^{-1}, 515 cm^{-1}, 629 cm^{-1}, 672 cm^{-1}, 765 cm^{-1}, 2367 cm^{-1}, 3316 cm^{-1}, 3399 cm^{-1}, 3474 cm^{-1}, and 3528 cm^{-1}. The formation of new class of hydrous bismuth oxide, named as HBO_3 can be easily verified through perusal of FTIR spectrum. As it has been already mentioned in introduction part that during synthesis comparatively larger quantity of NaOH was required for HBO_3 as compared with other HBOs (HBO_1 and HBO_2) then it is quite obvious that HBO_3 must possess more OH group. The absorption bands corresponding to wave numbers between 3300 cm^{-1} to 3600 cm^{-1} reveals characteristics of OH group.[36] HBO_3 shows four prominent peaks at wave numbers 3316 cm^{-1}, 3399 cm^{-1}, 3474 $cm^{-1}$and 3528 cm^{-1}, while other form of HBO such as HBO_1 reveals two OH peaks [21] and HBO_2 exhibits three peaks corresponds to OH group.[37] Hence the observation supports the formation of novel material termed as HBO_3. The absorption bands observed in the low frequency 400-800 cm^{-1} region of the spectrum are interpreted as the lattice vibration modes of metal-oxygen interaction hence confirm the involvement of Bi-O bond this observation is also supported by Fruth et al.[35] The absorption band between 2360 cm^{-1} to 2370 cm^{-1} is mainly attributed to the presence of carbonate as an impurity.[38]

3.2.3 Measurement of pH_{ZPC}

The pH_{ZPC} is an important interfacial parameter, which is extensively used in characterizing the ionization behavior of a surface. The plot of pH_i and pH_f for HBO_3 is found as shown in Fig.1c. The pH_{ZPC} of HBO_3 was found to be 7.5. Thus, on the basis of pH_{ZPC}, surface of the adsorbent is expected to be positively charged up to pH 7.5, which may be responsible for nitrate sorption from aqueous solutions.

3.2.4 Surface morphology of HBO_3 adsorbent

Surface morphology of HBO_3 was analyzed by Scanning Electron Microscopy (SEM). SEM images of the material's surface at 100x and 1000x magnification scales are shown in Fig. 4. While at 100x magnification, HBO_3 appears to have discrete granular particles of different sizes ranging from small to big, and at higher magnification (1000x); the surface appears cotton like spongy and porous. This roughness of surface may possibly be useful in nitrate sorption from aqueous solutions. The particle size distribution has been also investigated through SEM image analysis (Fig. 1d inset). The particle size seems to be highly inconsistent and heterogeneous in nature and size of particles was distributed in the range of 0-60 μm. The maximum number of particles was detected within 40-50 μm range. The EDS spectrum (Fig. 1e) reveals the presence of Bismuth and Oxygen atom which further validate the composition of as-synthesized HBO.

3.3Effect of solution pH on nitrate removal

Effect of solution pH on nitrate removal by HBO_3 was studied in 2.0-10.0 pH range and the results are given in fig. 2. The nitrate sorption capacity increases steadily from 0.056 mgN/g to 0.22 mgN/g with the increase of pH from 2.0 to 7.0 and then sorption capacity again dwindles to 0.037 mgN/g as the pH value reaches 10.0. Thus maximum removal of nitrate by HBO_3 was observed at pH 7.0 which indicates that performance of adsorbent is highly effective in neutral pH. This observation can be illustrated on the basis of pH_{ZPC}, as the surface of the adsorbent likely to be positively charged at pH < pH_{ZPC}, the pH_{ZPC} of HBO_3 was found to be 7.5. It means that at pH 7.0 the adsorbent surface is highly protonated which favored binding of negatively charged nitrate ions electrostatically. However poor uptake of nitrate ions in the protonated medium could be attributed to reduced availability of free anions as a result of formation of HNO_3.[18] While in alkaline medium (pH >7) the presence of large amount of hydroxyl ions in the aqueous solution starts competing with the nitrate ions for binding with the surface active sites which results in meager sorption of nitrate ions.

3.4Kinetic studies

Adsorption is time-dependent process and it is important to know the rate of adsorption to design treatment plants and evaluate the efficiency of the adsorbent for removal of pollutant species from solutions[39]. The kinetics of nitrate removal by HBO_3 for initial nitrate concentrations in 14-56 mgN/L range was studied by varying the contact time from 5-420 min. Fig. 3a shows the nitrate removal potential of HBO_3 with time and at four initial nitrate concentrations. From Fig. 3a it is observed that nitrate removal potential, q_t (mgN/g) of HBO_3 increases with increasing contact time, t. For the selected concentration levels of nitrate, a contact time of 3 h appears reasonable, beyond which the increase in q_t with time is rather marginal. However complete equilibrium seems to be attained at 300 min of contact time. The adsorption potential (q_t) generally increases with increasing initial nitrate concentrations for all durations. For HBO_3, q_t increased from 0.052 mgN/g (at 40 min and 14 mgN/L) solution to 0.299 mgN/g (at 360 min and 56 mgN/L) by varying (increasing) initial nitrate concentrations at 14, 28, 42 and 56 mgN/L.

The kinetic parameter for adsorption of nitrate on HBO_3 was evaluated using two widely used pseudo-first order[40] and pseudo-second order[41] kinetic model. Pseudo-first order adsorption kinetic expression given as[35]:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \tag{3}$$

where, q_e and q_t are the amount of nitrate adsorbed (mgN/g) at equilibrium and at any time, t respectively. The adsorption rate constant k_1 can be determined from the slope of the linear plot of log ($q_e - q_t$) versus t.

It has been found that the resultant plots for all initial anion concentration deviates significantly from its linearity besides poor correlation coefficient values and inconsistency between experimental and calculated values of q_e recommends that pseudo-first order kinetics model is not suitable in explaining sorption kinetics data. Therefore sorption data was further treated by means of pseudo-second order kinetics model. The expression for pseudo-second order kinetics given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where k_2 (g/mg.min) is the second order rate constant which can be calculated from the intercept of the graph plotted between t/q_t and t. The pseudo-second order profile given in fig. 3b, the plot maintains reasonable linearity for given time period at all nitrate concentrations. Moreover high correlation coefficient values and comparable experimental and calculated q_e values undoubtedly suggest that nitrate sorption kinetics can be approximated as pseudo-second order kinetics. The parameters calculated for pseudo-first order and pseudo-second order given in Table 1. From the table it has been observed that the rate constant values calculated for both pseudo-first order and pseudo-second order kinetics model seems to follow decreasing trend with the rise of initial nitrate concentration the reason behind this trend anticipated on the basis of availability of active sites on adsorbent material required for the binding of nitrate ions. In case of low nitrate ion concentration there were few nitrate ions in liquid phase and therefore gets easily accommodated on the freshly available reactive sites of HBO_3. However with the increase of initial concentration the binding site starts quenching and consequently few reactive sites were available for the interaction with nitrate ions which leads to decrease in rate constant values with the rise of nitrate ion concentration.

3.5 Mechanism of nitrate removal by HBO_3

In order to gain deep insight for removal mechanism of nitrate ions from aqueous solutions it is required to treat the sorption kinetics data with two important mathematical model proposed by Weber- Morris and Boyd et al.

3.5.1 Weber–Morris model

Weber–Morris model is used to interpret the role of intra particle diffusion of solute in adsorbent. The Weber–Morris model is expressed as follows[42]:

$$q_t = k_{id}\, t^{0.5} + C \qquad (5)$$

Where k_{id} is intra particle diffusion rate constant, obtained from slope and C is the intercept of the plot of q_t versus $t^{0.5}$ (Fig. 3c). The parameters are provided in Table 1. The model assumes that if plot bears straight line and passes through the origin then sorption is controlled by pore diffusion and solute ions diffuse within the pores and capillaries of the adsorbent material [43] but if plot fails to maintain linearity then film diffusion process considered to be the rate limiting. In present case plots obtained for intra particle diffusion at different nitrate concentration seems to exhibit multiple straight lines which demonstrate about the involvement of multistage adsorption. The intra-particle diffusion curve appears to be divided into three distinct linear regions. The first curve that obtained during the initial time period of 5 to 40 minutes indicates external mass transfer which involve transportation of nitrate ions from liquid phase to solid boundary of the adsorbent; the second curve at 60 to 180 minutes attributed to film diffusion process and the third curve at a longer time period of 240 to 360 minutes represents gradual adsorption stage which is dominated by pore diffusion process. Overall it becomes quite clear that adsorption of nitrate ions is not completed in one step rather it is a complex process in which more than one mechanism dictate the sorption process[44-45].

3.5.2Boyd kinetic expression

As from the intra-particle diffusion study it becomes evident that sorption of nitrate ions on HBO_3 is a complex and multi-stage process. But the process which controls the overall rate of sorption process remains uncertain which needs to be addressed. Therefore in order to determine the actual rate limiting step a complex mathematical expression given by Boyd et al. have been applied to the sorption kinetics data. The Boyd[46] expression is represented as:

$$G = 1 - \frac{6}{\pi^2}\exp(-B_t) \tag{6}$$

where *G* is the fraction of solute adsorbed at time, *t* is given by:

$$G = \frac{q_t}{q_e} \tag{7}$$

where, q_t and q_e are the amounts of nitrate adsorbed at time *t* and at infinite time (equilibrium), substituting Eq. (6) into Eq. (5), the kinetic expression can be written as follows:

$$B_t = -0.4977 - \ln\left(1 - \frac{q_t}{q_e}\right) \tag{8}$$

The B_t values were calculated using relation (7) and the values obtained for different nitrate concentrations were plotted against time, *t* (Fig.3d). The resultant slope of the plot was used to calculate *B* values for the determination of effective diffusion coefficient, D_i (cm^2/s) using the relation given as.

$$B = \frac{\pi \, Di}{r^2} \qquad (9)$$

where, D_i is the effective diffusion coefficient of adsorbate, and r the radius of adsorbent particle assumed to be spherical.

The nature of the plots obtained from the Boyd model conveyed important related to determination of rate limiting step of the sorption process. Accordingly, if plot is linear and passes through the origin then particle diffusion considered to be rate limiting however in case if plot is linear but do not pass through the origin then external mass transfer governs the overall rate of removal process[47]. In this study all the plots for different nitrate ion concentration provided linear relationship, none of the line segment passes through the origin. Thus, film diffusion seems to be controlling the overall rate of the nitrate sorption on HBO_3. The correlation coefficient (R^2) for linearity of (B_t) and t values at different nitrate concentrations of 14, 28, 42 and 56 mg N/L are found to be 0.983, 0.991, 0.968 and 0.871 respectively. Thus, all plots may broadly be taken as linear, but they do not appear to pass through origin. Thus, film diffusion or chemical reactions seem to be governing the sorption rate of nitrate on HBO_3. The effective diffusion coefficient (D_i) values for different nitrate ion concentration were also calculated and given in Table. 1. The values obtained for effective diffusion coefficient also helps in distinguishing between pore diffusion and film diffusion process. The process would be film diffusion if D_i is in the range of 10^{-6}-10^{-8} cm^2/sec and for pore diffusion D_i should be in the range 10^{-11} to $10^{-13}$$cm^2$/sec.[47] In this study the values of D_i were observed to be around 10^{-8} cm^2/sec which clearly proposed that film diffusion process is the rate controlling step for nitrate sorption on HBO_3.

The *Di* values seem to be increases with nitrate concentration which can be elucidate on the basis of concentration gradient. At low nitrate concentration diffusion rate is lower due to low concentration gradient as rate scales with the concentration gradient but with the increase of nitrate concentration the concentration gradient experiences change and to maintain balance between the adsorbate present on the solid surface and near boundary layer of adsorbent which results in increase in diffusion rate.[48]

3.5 Effect of temperature on nitrate sorption

In order to study the effect of temperature on nitrate removal by HBO_3, experiments were carried out to find sorption of nitrate at 14, 28 and 42 mgN/L of initial nitrate concentration at 293, 303 and 313 K. Fig.4a shows the variation of nitrate adsorption potential (q_e) of $HBO_3$with temperature at different initial nitrate concentrations. It has been found that for all concentration uptake capacity of HBO_3 for nitrate ions augmented steadily at elevating temperature from 293 K to 313 K. This indicated that high temperature favors nitrate sorption on HBO_3 which further represent endothermic nature of adsorption process. The reason behind increase in the adsorption efficiency at elevated temperatures may be due to increase in the binding tendency of nitrate ions with the active sites of HBO_3 that result in strengthening the extent of adsorption.[18] Similar observations have been reported by Islam et al.[44] for nitrate removal by hydroxyapatite .

3.6Adsorption isotherm studies

Adsorption isotherms are used to understand the mechanism and distribution of the adsorbate between the liquid and solid adsorbent phase at equilibrium during the process of removal. Langmuir, Freundlich and Dubinin–Radushkevich (D-R) isotherm models are most commonly used for sorption studies.[44] The experimental data of nitrate sorption by $HBO_3$for different initial concentrations as well as temperature were plotted in linearized forms of Langmuir, Freundlich and D-R sorption isotherms.

3.6.1 Langmuir isotherm

Langmuir equation is valid for monolayer sorption on adsorbent surface with finite number of identical sites and its linear form is given by the following equation: [49]

$$\frac{1}{q_e} = \left(\frac{1}{q^0 b}\right)\frac{1}{C_e} + \frac{1}{q^0} \qquad (10)$$

where, q^0 is maximum amount of the adsorbate per unit weight (mg/g) of adsorbent to form a complete monolayer on the surface (adsorption capacity), C_e is equilibrium concentration of adsorbate, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g) and b is the binding energy constant. Fig. 4b shows the linearised plot of nitrate sorption data by HBO_3 for Langmuir adsorption isotherm. The initial concentration of nitrate in solution varied from14 mgN/L to 84 mgN/L.

The high correlation coefficient (R^2) values for the plots indicating good agreement of nitrate sorption data with linearised model of Langmuir adsorption isotherm. From fig. 4b , the maximum adsorption capacity (q^0) was estimated to be 0.97 mgN/g. The increasing values of q^0 (Table 2) with increasing temperature indicates higher temperature augments the nitrate sorption capacity of HBO_3. The increasing values of b with temperature suggest increasing bonding energy of nitrate with HBO_3 media at higher temperatures, reaffirming the endothermic character of the process.

3.6.2 Freundlich isotherm

Freundlich isotherm model can be applied for non-ideal adsorption on heterogeneous surfaces as well as multilayer sorption. Mathematically, the linear form of Freundlich[50] equation is expressed as:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (11)$$

where, q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of nitrate (mgN/L), n is the Freundlich constant indicates the degree of favorability of adsorption and

K_F is isotherm constant. Fig. 4c shows the plot of log C_e vs log q_e for nitrate sorption on HBO_3 for linear form of Freundlich isotherm. The higher correlation coefficient (R^2) values obtained for the plot at three different temperatures suggests good fit for sorption data in Freundlich model. The values of n are found as 1.61, 2.31 and 2.91. Commonly, the value of n in between 1 and 10 shows beneficial adsorption[10]. In present case all n values are greater than 1 which advocates that adsorption of nitrate on HBO_3 is beneficial. The increasing values of K_F with temperature further indicate that adsorption becomes more favorable with increasing temperature. The suitability of Freundlich isotherm model also implies presence of heterogeneous sorption sites on adsorbent surface and nitrate sorption takes place in multilayered manner over the reactive sites of adsorbent.

3.6.3 Dubinin-Radushkevich (D-R) isotherm

In order to understand the type of adsorption, whether physical or chemical, equilibrium data for nitrate sorption on HBO_3were also tested with D-R isotherm, as Langmuir and Freundlich adsorption isotherm constant do not provide any idea about the adsorption mechanisms[44]. The linearised form of D-R[51] equation is given below:

$$\ln q_e = \ln q_m - K\varepsilon^2 \qquad (12)$$

where, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent, q_m is the theoretical adsorption capacity, K is the constant related to adsorption energy, and ε is Polanyi potential, which can be calculated by using equation:

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \qquad (13)$$

where, R is universal gas constant (8.314 KJ mol/K), T is the absolute temperature in Kelvin, C_e is the equilibrium concentration of adsorbate (mgN/L) in solution.

Fig.4d shows the D-R isotherm plot of ln q_e against ε^2 for nitrate sorption on HBO_3. The correlation coefficients (R^2) values obtained for three selected temperatures found to be in range of 0.77- 0.86. The poor R^2 values recommend non applicability of D-R model in interpreting equilibrium data of HBO_3 for nitrate adsorption. The values of D-R isotherm constants K (mol^2/J^2) and q_m (mg/g) were calculated from the slope and intercept of the plot respectively. The mean adsorption energy (E) was calculated from the constant K using the relation given below: [44]

$$\mathrm{E} = (2\mathrm{K})^{-1/2} \qquad (14)$$

The mean adsorption energy (E) is used to classify the process of adsorption into chemical adsorption and ion exchange. If the value of E falls in between 8 and 16 k/mol, the adsorption process is said to be chemical adsorption, while the value below 8 kJ/mol indicates the physical adsorption.[52] From the D-R isotherm the values of E are found to be 0.221, 0.387 and 0.581 kJ/mol respectively, which is related to the physical adsorption. Therefore obtained values for mean adsorption energy fairly indicates about the scope of regeneration of the used adsorbent as adsorbent regeneration truly depends on adsorbate-adsorbent interaction and the possibility of regeneration enhances if physical adsorption is the prevailing phenomena[10].

Parameters calculated from Langmuir, Freundlich and D-R isotherm equations with corresponding correlation coefficient (R^2) values for nitrate adsorption on HBO_3 are presented in Table 2.

3.7 Thermodynamic studies

Studies of thermodynamic parameters are helpful to understand the adsorption process in a better way. In present study, thermodynamic parameters in terms of changes in Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were determined as per the eq., (14) and (15) [48]

$$\ln b = \Delta S^{\circ}/R - \Delta H^{\circ}/RT \qquad (15)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\,\Delta S^{\circ} \qquad (16)$$

where b is the Langmuir constant in L/g, R is the universal gas constant (8.314 J/mol K), and T is the absolute temperature (K).

Table 3 summarizes the thermodynamic parameters determined for nitrate adsorption on HBO_3 at the temperatures 293, 303 and 313 K temperatures. From Table 3, it is observed that values of Gibbs free energy change (ΔG^0) are found negative for adsorption of nitrate on HBO_3 (at 293, 303 and 313 K temperatures respectively).The negative values of Gibbs free energy changes indicate feasibility and spontaneous nature of adsorption process.[48] The magnitudes of ΔG^0 for adsorption of nitrate on HBO_3 are found increasing with increasing temperatures indicating more spontaneity of adsorption at higher temperature.[38] Similar observations reported for nitrate adsorption on hydroxyapatite by Islam et al.[44] The positive values of enthalpy change once again confirm endothermic nature of sorption process.

3.8 Effect of competing anions

In order to investigate the effect of competitive anions such as sulfate, bicarbonate, and chloride on sorption capacity of nitrate ions from aqueous solution by HBO_3, the concentration of these anions were varied from 1.0 meq/L to 5.0 meq/L and nitrate removal (%) at 1.0 meq/L was observed and results of the experiments were depicted in fig.5. It can be observed from the figure that the sulfate ions imposed relatively greater negative impact for nitrate ion sorption which is further followed by bicarbonate and chloride ions respectively. This mostly happen because multivalent anions possess high charge density as compared to monovalent ions therefore actively competes for available binding sites on adsorbent.[18, 53] The order of anions reducing the removal of nitrate by HBO_3 is observed as SO_4^{2-}> HCO^{3-}> Cl^-. The sorption capacity of HBO_3 for nitrate ions with initial nitrate concentration of 14mgN/L remarkably decreases from, 0.22 mgN/g to 0.097, 0.066

and 0.037 mgN/g in presence of SO_4^{2-}, HCO_3^- and Cl^- respectively at 5.0 meq/L of anion concentration.

3.9 Performance of HBO media in removal of nitrate from groundwater samples

Srivastav et al.[54] examined total 45 groundwater samples (30 from open wells and 15 from tube wells) which is being used for drinking purpose by the people of Varanasi and other adjoining areas, Uttar-Pradesh (India). These groundwater samples were analyzed for nitrate concentrations along with other physico-chemical water quality parameters such as temperature, pH, turbidity, total dissolved solids (TDS), alkalinity, dissolved oxygen, chloride and sulfate. Nitrate concentration in open well groundwater samples at five locations (namely *Harhuan, Kharion, Khardu, Sindhora and Chiraigaon*) were exceeded the prescribed limit (<45 $mgNO_3^-/L$ of Indian standard), there the range of nitrate was found in between 47 to 68 $mgNO_3^-/L$, whereas, in tube well groundwater samples (*Shivpur* location) the nitrate concentration was found about 47 $mgNO_3^-/L$ which was also above permissible limit. Five sites such as *Barchhawan Shahansapur, Thatra, Lohta and Sandaha* were also vulnerable because the concentration of nitrate in the ground waters was in the range of 36 to 43 $mgNO_3^-/L$ which possibly increase in the forthcoming years.

According to a report of Central Ground Water Board (CGWB) [55], Ministry of Water Resources, Government of India, around 14 districts of nine (09) Indian states, where groundwater was found contaminated by both of nitrate (up to 105 $mgNO_3^-/L$) and fluoride (up to 2.8 mg/L) for drinking purpose.[55]

Hence, an experiment was conducted on the groundwater samples of Indian Institute of Technology (Banaras Hindu University), Varanasi campus to examine the applicability of mixed HBO media in field conditions. Firstly, physico-chemical parameters of groundwater samples of campus were analyzed and the result is given in Table 4. These water samples were used in batch adsorption experiments to know the performance of mixed HBO media. As we have already reported in our earlier communication that HBO_1 has very good potential of removal of fluoride from aqueous solutions.[21]

In this experiment HBO_1 and HBO_3 powders were mixed in equal proportions to prepare a single adsorbent. Powder dosage of 50 g/L was taken for 3 h of contact time with continuous shaking. The filtered samples were analyzed for final pH, nitrate, fluoride, sulfate and bicarbonate concentrations and results are given in Table 4. From the Table, it has been observed that the pH of treated water is marginally reduced from 7.9 to 7.3 after treatment. Sulfate and bicarbonate concentrations are also reduced by 50% and 76% respectively. The nitrate concentration is reduced from 60.2 $mgNO_3^-/L$ to 12.8 $mgNO_3^-/L$, whereas fluoride concentration decreased from 4.0 mg/L to 1.3 mg/L. The results irrefutably specifies that mixed media prepared from HBO_1 and HBO_3 exhibits appreciable capability for scavenging nitrate and fluoride ions along with bicarbonate and sulfate ions from groundwater samples. All the tested parameters in treated water were found within permissible range of drinking water as per the Indian standard.

4. Conclusions

Nitrate contamination of ground water is a worldwide problem. Application of hydrous bismuth oxides (HBOs) has been reported in the present paper for nitrate removal from aqueous solutions. Some of the important conclusions from the observations and analyses made in present study are as follows:

- Three forms of HBOs (designated as HBO_1, HBO_2 and HBO_3) have been synthesized and were used as an adsorbent for the removal of NO_3^- from aqueous phase.

- Among all the three HBOs, HBO_3 was observed to show highest nitrate sorption potential from aqueous solutions.
- XRD analysis of the synthesized material HBO_3 indicated crystalline nature of the material and FTIR analysis confirms formation of new class of HBO represented as HBO_3 which comprises of enhanced hydroxyl character.
- The SEM images of HBO_3 shows rough surface containing grain like structure.
- The pH of treated water was found around 7.5 indicating non-involvement of hydroxyl ion as replacement for nitrate removal by HBO_3 adsorbent.
- The nitrate adsorption process agrees well with pseudo-first-order kinetic model.
- To gain deep insight for removal mechanism Weber-Morris and Boyd model were explored.
- Weber-Morris model conveys that film diffusion and pore diffusion both plays significant role in the sorption process while Boyd model confirms that external mass transfer mainly governs the rate limiting process for adsorption of nitrate ions on HBO_3.
- Based on coefficient of correlation (R^2) values Freundlich isotherm better represent the sorption equilibrium data, indicating adsorption of nitrate occurs in multilayer.
- The values of mean adsorption energy (E) calculated from D–R isotherm is less than 8 kJ/mol, indicating physical adsorption of nitrate on HBO_3.
- The negative values of Gibbs free energy change (ΔG^0) indicate the feasibility and spontaneous nature of adsorption process.
- The positive values of enthalpy changes (ΔH^0) confirmed the endothermic nature of nitrate sorption process.

- Among the commonly available competitive anions, sulfate ions drastically retards sorption performance of HBO_3 for nitrate ions.
- The performance of mixed proportions of HBO_1 and HBO_3adsorbents was also tested and found suitable to reduce nitrate and other anions and bring it up to the potable range.
- Hydrous bismuth oxide in the form of HBO_3 appears to have good potential for nitrate removal from aqueous solutions as well as from ground waters.

Acknowledgements: The authors are thankful to Department of Science and Technology (DST), Government of India for providing financial support. Thanks are also due to anonymous reviewers for their comments and suggestion.

References

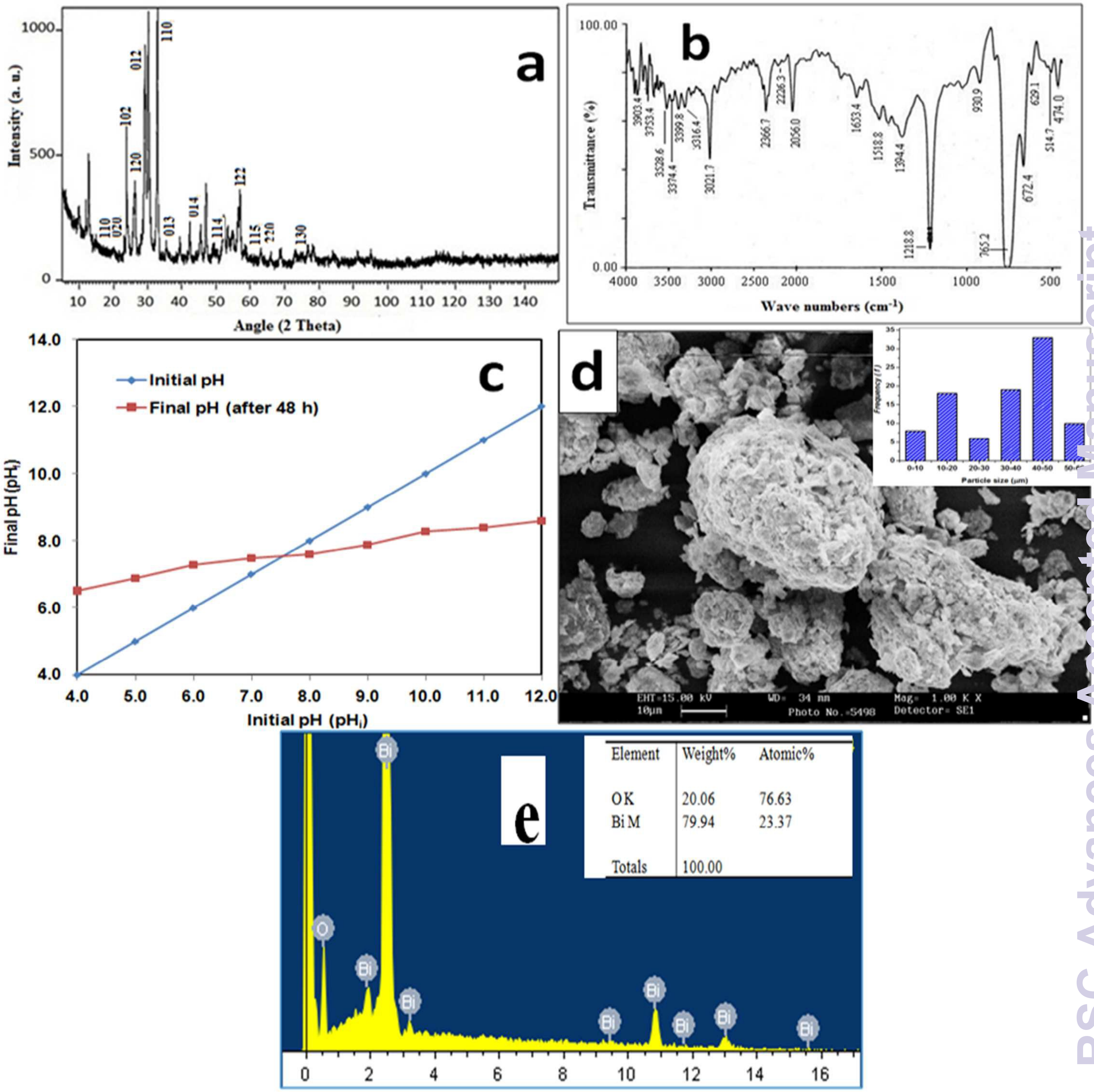
1. P. K. Singh, A. L. Srivastav, D. K .Ghosh and Y. C. Sharma, *Desal Water Treat*, 2012, **40 (1-3),** 144-152.
2. C. Noubactep, *Chem Engg J*, 2010, **165**, 740–749.
3. J. N. Galloway, A. R. Townsend, J. W. Erisman, M. Bekunda, Z. C. Cai, J. R. Freney, L. A. Martinelli, S. P. Seitzinger and M. A. Sutton, *Science*, 2008, **320**, 889–892.
4. H. Zhang and K. M. Hiscock, *J Hydrol*, 2011, **399**, 212–225.
5. H. H. Comly, *JAMA, 257(20) (1987)* 2788–2792.
6. M. Trevisan, L. Padovani and E. Capri, *J Environ Manage,* 2000, **26(5)**, 577-584.
7. Bureau of Indian Standards (BIS), *Specifications for Drinking Water. IS: 10500:1991*, New Delhi, 1991/2003.
8. WHO (World Health Organization) *Guidelines for drinking-water quality, 3rd ed. Recommendations.* ***Vol. 1,*** *Geneva*, 2008.
9. J. J. Schoeman and A. Steyn, *Desal*, 2003, **155**, 15–26.
10. S. N. Milmile, J. V. Pande, S. Karmakar, A. Bansiwal, T. Chakrabarti and R. B. Biniwale, *Desal*, 2011, **276 (1-3),** 38-44.

11. N. Barrabes and J. Sa, *Appl Cataly B: Environ*, 2011, **104**, 1–5.
12. M. A. Hasnat, N. Ahamad, S. M. NizamUddin and N. Mohamed, *Appl Surf Sci*, 2012, **258**, 3309– 3314.
13. V. Srivastava, C.H. Weng, V.K. Singh, Y.C. Sharma, *J. Chem. Engg. Data*, 2011, **56,** 1414-1422.
14. Y.C. Sharma, B. Singh, A. Agrawal, C.H. Weng, *J. hazardous Mat.*, 2008, 151, 789-93.
15. A. Bhatnagar and M. Sillanpa, *Chem Engg J*, 2011, **168,** 493-504.
16. Y.C. Sharma, Uma, A.S.K. Sinha, S.N. Upadhyay, *J. Chem. Engg. Data*, 2010, 55,2662-2667.
17. N. Viswanathan and S. Meenakshi, *Appl Clay Sci*, 2010, **48,** 607–611.
18. M. Mohapatra, D. Hariprasad, L. Mohapatra, S. Anand and B. K. Mishra, *App Surf Sci*, 2012**,258**, 4228-4236.
19. V. H. Montoya, L. A. R. Montoya, A. B. Petriciolet and M. A. M. Morán, *Biochem Engg J,* 2012, **62**, 1–7.
20. M. Mourabet, A. ElRhilassi, H. ElBoujaady, M. Bennani-Ziatni, R. ElHamri and A. Taitai, *App Surf Sci*, 2012, **258 (10),** 4402-4410.
21. A. L. Srivastav, P. K. Singh, V. Srivastava and Y. C. Sharma, *J Hazard Mater,* 2013a, **263,** 342-352.
22. M. Szlachta, V. Gerda and N. Chubar, *J Coll Interf Sci*, 2012, **365,** 213–221.
23. S. Luther, N. Borgfeld, J. Kim and J. G. Parsons, *Microchemi J*, 2012, **101,** 30–36.
24. M. Abe and I. Ito, *Nippon Kagaku Zasshi*, 1965, **86,** 817.
25. A. Bhatnagar, E. Kumar and M. Sillanpa, *Chem Engg J*, 2010, **163**, 317-323.
26. U. Fritsche, *J Enviro Sci Health, A*, 1993, **28**, 1903-1913.
27. P. K. Singh and D. K. Ghosh, In: B. B. Jana, R. D. Banerjee, B. Guterstam, J. Heeb (Eds.) Waste Recycling and Resource Management in the Developing World, *India and International Ecological Engineering Society, Switzerland*, 2000.
28. P. Babula, V. Adam, R. Opatrilova, J. Zehnalek, L. Havel and R. Kizek, *Environ Chem Lett*, 2008, **6**, 189-213.
29. Y. Ma, L. Kuang, X. He, W. Bai, Y. Ding, Z. Zhang, Y. Zhao and Z. Chai, *Chemosphere*, 2010, **78**, 273–279.
30. S. Tripathi, S. K. Sonkar and S. Sarkar, *Nanoscale*, 2011, **3**, 1176-1181.

31. T. Zhai, S. Xie, X. Lu, L. Xiang, M. Yu, W. Li, C. Liang, C. Mo, F. Zeng, T. Luan, and Y. Tong, *Langmuir*, 2012, **28**, 11078−11085.
32. Standard Methods for the Examination of Water and Wastewaters, 20th ed. *American Public Health Association (APHA)*, *Washington*, D.C. 1998.
33. Y. C. Sharma, Uma and S. N. Upadhyay, *En Fuels,* 2009, **23**, 2983–2988.
34. P. Xiao, L. Zhu, Y. Zhu and Y. Qian, *J. Solid State Chem*, 2011, **184**, 1459-1464.
35. V. Fruth, M. Popa, D. Berger, C. M. Ionica and M. Jitianu, *J Eur Ceram Soc*, 2004, **24 (6)**, 1295–1299.
36. E. Diez, O. Monnereau, L. Tortet, G. Vacquier, P. Llewellin and F. Rouquerol, *J Optoele Adv Mater*, 2000, **2**, 552-556.
37. A. L. Srivastav, P. K. Singh and Y. C .Sharma, *Desalin Water Treatment*, doi: 10.1080/19443994.2014.938251.
38. K. Biswas, K. Gupta, A. Goswami and U. C. Ghosh, *Desalin*, 2010, **255,** 44-51.
39. Z. Zawani, C. A. Luqman and S. Y. C. Thomas, *European J Scienti Res*, 2009, **37 (1)**, 63-71.
40. S. Lagergren, *K. Sven.Vetenskapsakad. Handl.,* 1898, **244**, 1.
41. Y. S. Ho, *Adsorption*, 2004, **10**,151.
42. W. J. Weber and J.C. Morris, *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.,* 1963, **89**, 31.
43. M. G. Sujana and S. Mohanty, *Inter J Engg Sci Tech,* 2010, **2 (8)**, 1-12.
44. M. Islam, P. C. Mishra and R. K. Patel, *J Enviro Manage*, 2010, **91,** 1883-1891.
45. S. S. Gupta and K. G. Bhattacharyya, *Adv Coll Inter Sci*, 2011, **162**, 39–58.
46. G. E. Boyd, A. W. Adamson Jr and L. S. Myers, *J Am Chem Soc*, 1947, **69**, 2836–2848.
47. S. Banerjee, G. C. Sharma, M.C. Chattopadhyaya and Y. C. Sharma, *J Environ Chem Eng,* 2014, **2**, 1870–1880.
48. S. Banerjee, R. K. Gautam, A. Jaiswal, M. C. Chattopadhyaya and Y. C. Sharma, *RSC Adv.* 2015, **5**, 14425–14440.
49. I. Langmuir, *J. Am. Chem. Soc.* 1916, **38**, 2221.
50. H.M.F. Freundlich, *J. Phys. Chem.*, 1906, **57**, 385.
51. M. M. Dubinin, *Chem. Rev.* 1960, **60**, 931–937.
52. S. K. Swain, S. Mishra, T. Patnaik, R. K. Patel, U. Jha and R. K. Dey, *Chem Engg J*, 2012, **184**, 72– 81.
53. W. Li, C. Y. Cao, L. Y. Wu, M. F. Ge and W. G. Song, *J Hazard Mater,* 2011, **198**,143-150.

54. A. L. Srivastav, V. K. Dubey, P. K. Singh and Y. C. Sharma, *J Indian Chem Soc*, 2013c, **90**, 983-989.

55. CGWB (Central Ground Water Board). A report of Central Ground Water Board, *Ministry of Water Resources; Government of India*, 2010.



Element	Weight%	Atomic%
O K	20.06	76.63
Bi M	79.94	23.37
Totals	100.00	

Fig. 1 (a) FTIR spectra of HBO_3 (b) XRD diffractogram of HBO_3 (c) pH_{ZPC} of HBO_3 (d) SEM micrograph of HBO_3 at resolution of 1.0 KX (inset: particle size distribution of HBO_3) (e) EDS spectra of HBO_3.

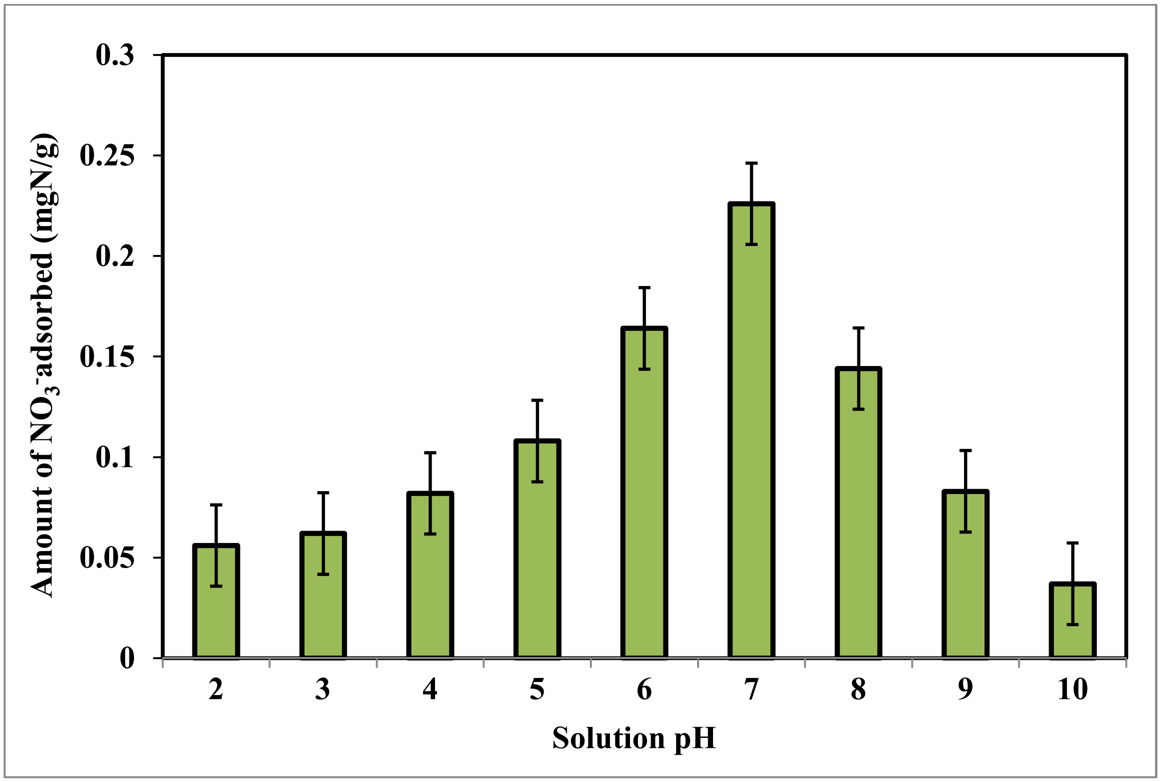


Fig. 2 Effect of solution pH on nitrate removal (Initial nitrate concentration=14 mgN/L, adsorbent dosage=50 g/L, Contact time=3 h).

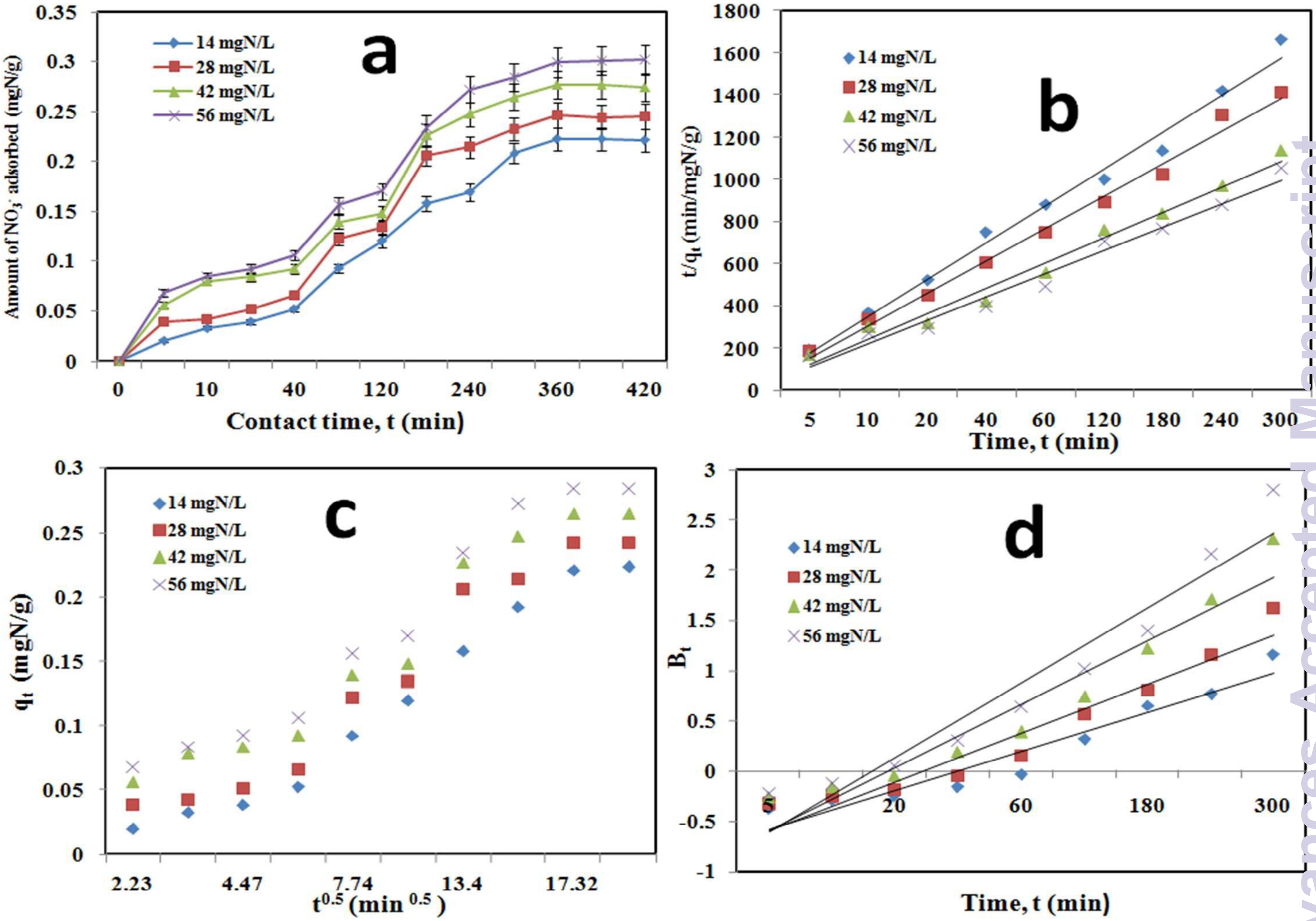


Fig. 3 (a) Variation of adsorption capacity (q_t) with contact time (b) pseudo-second order kinetic plots at different initial nitrate concentration (c) intra-particle diffusion plots at different initial nitrate concentrations (d) Boyd plots for nitrate sorption at different initial nitrate concentrations.

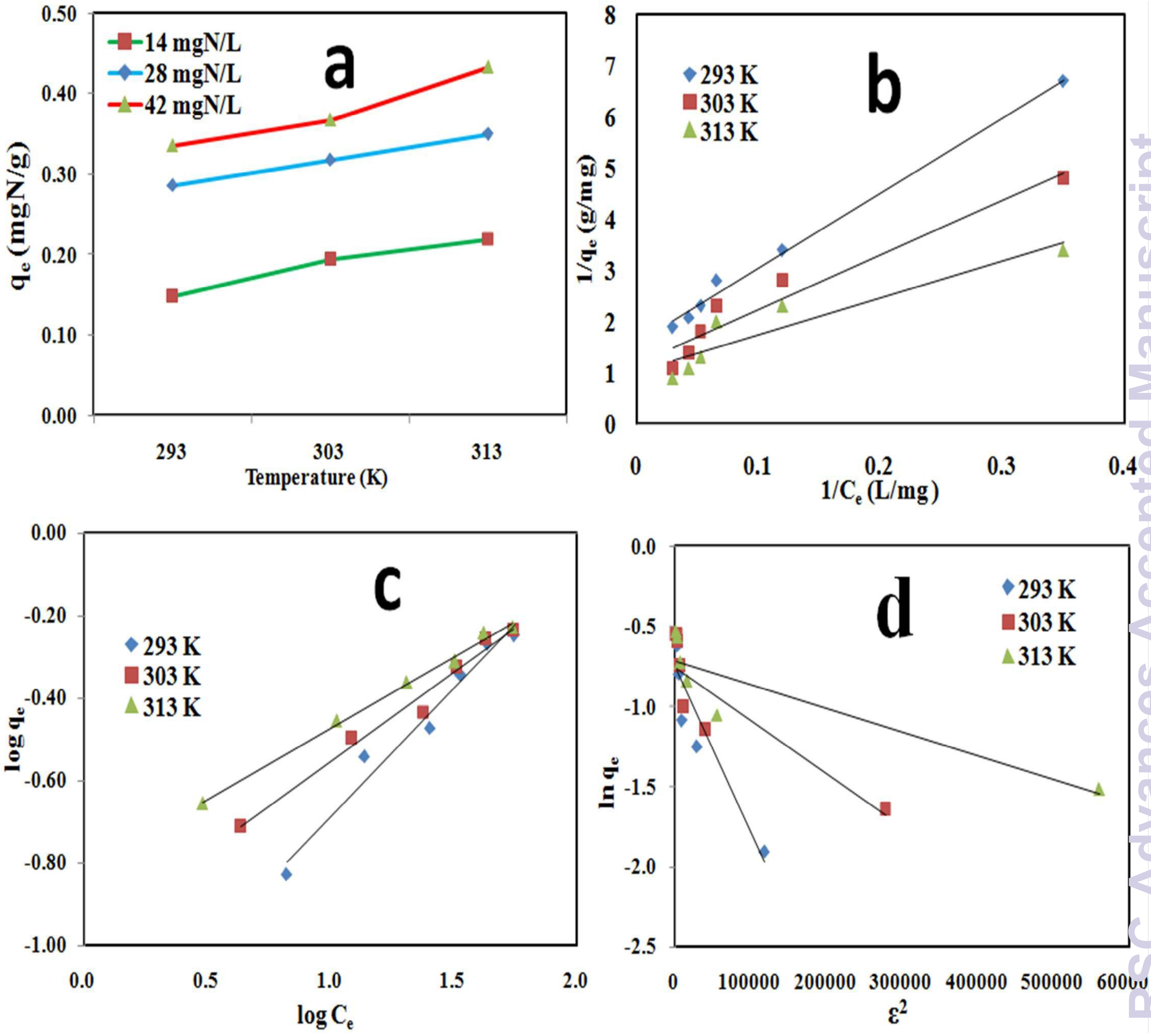


Fig. 4 (a) Effect of temperature on nitrate sorption on HBO_3 at three different initial nitrate concentrations (b) Langmuir isotherm plots for nitrate sorption at three different temperatures (c) Freundlich isotherm plots for nitrate sorption at three different temperatures (d) D-R isotherm plots for nitrate sorption at three different temperatures.

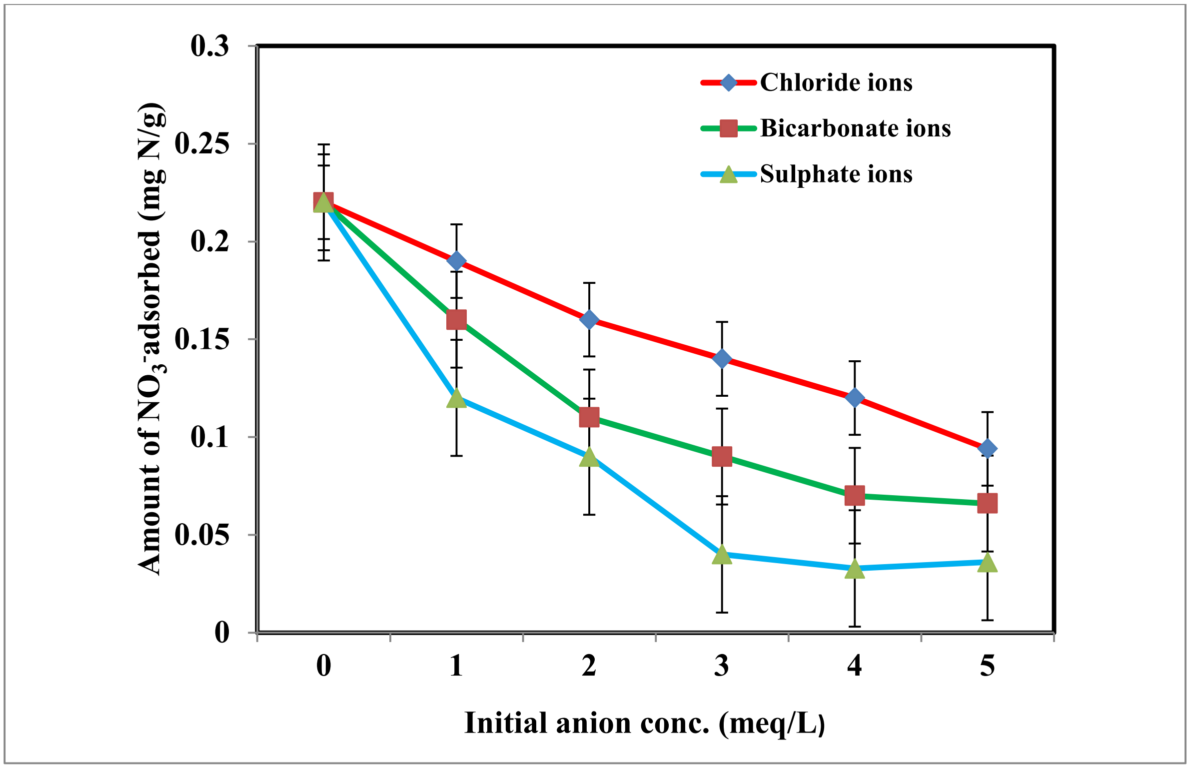


Fig. 5 Effect of competing anions on sorption of nitrate from water by HBO_3 at 313 K.

Pseudo First Order Model	14 mgN/L	28 mgN/L	42 mgN/L	56 mgN/L
k_1 (min^{-1})	0.47	0.41	0.35	0.32
$q_{e\,(\mathrm{exp})}$(mgN/g)	0.18	0.22	0.26	0.29
$q_{e\,(\mathrm{cal})}$ (mgN/g)	0.56	0.59	0.61	0.63
R^2	0.807	0.813	0.802	0.807

Pseudo Second Order Model	14 mgN/L	28 mgN/L	42 mgN/L	56 mgN/L
k_2 (g min^{-1}mg^{-1})	0.22	0.16	0.15	0.12
$q_{e\,(\mathrm{cal})}$ (mgN/g)	0.16	0.20	0.22	0.27
R^2	0.988	0.991	0.979	0.978

Intra-particle diffusion model	14 mgN/L	28 mgN/L	42 mgN/L	56 mgN/L
$k_{id,1}$ (mg/g.min$^{0.5}$)	0.012	0.011	0.009	0.008
C_1	0.010	0.027	0.049	0.057
R^2	0.985	0.891	0.918	0.981
$k_{id,2}$(mg/g.min$^{0.5}$)	0.043	0.039	0.035	0.032
C_2	0.058	0.072	0.108	0.084
R^2	0.990	0.854	0.879	0.826
$k_{\mathrm{id},3}$(mg/g.min$^{0.5}$)	0.008	0.009	0.006	0.004
C_3	0.186	0.208	0.241	0.268
R^2	0.823	0.818	0.856	0.820

Boyd Kinetic model	14 mgN/L	28 mgN/L	42 mgN/L	56 mgN/L
B (sec^{-1})	1.94	2.43	3.16	3.27
D_i ×10^{-8} (cm^2 sec^{-1})	3.86	4.83	6.28	6.51

Table 1 Kinetics parameters for nitrate sorption on HBO_3 at different initial nitrate concentration at 313 K.

Temp. (K)	**Langmuir parameters**			**Freundlich parameters**			**D-R parameters**		
	q^0 (mgN/g)	**b** (L/g)	**R^2**	**K_F** (mgN/g)	**n**	**R^2**	**q_m** (mgN/g)	**E** (kJ/mol)	**R^2**
293	0.64	0.10	0.994	0.100	1.61	0.970	0.47	0.221	0.865
303	0.84	0.11	0.941	0.103	2.31	0.982	0.46	0.387	0.777
313	0.97	0.14	0.855	0.152	2.91	0.995	0.49	0.581	0.800

Table 2 Isotherm parameters for Langmuir, Freundlich and D-R models at different temperatures.

Temperature (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol/K)
293	-55.05	13.96	28.38
303	-57.53		
313	-59.89		

Table 3: Thermodynamic parameters for nitrate adsorption on HBO_3.

Parameters	Characteristics of groundwater	Characteristics of treated groundwater
pH	7.9	7.3
Sulfate (mg/L)	16.0	8.0
Bicarbonate (mgCaCO$_3$/L)	296.0	70.0
Nitrate (mgNO$_3^-$/L)	60.2	12.8
Fluoride (mg/L)	4.0	1.3

Table 4 Performance of mixed HBO media with groundwater samples.