

A New and Successful Utilization of Egyptalum Company Solid Waste in Adsorptive Removal of Nitrates from Water Supplies

S. El-Nahas^{1*}, H. M. A. Salman¹ and W. A. M. Seleem¹

¹Department of Chemistry, Faculty of Science, South Valley University, 83523 Qena, Egypt.

Authors' contributions

This work was carried out in collaboration between all authors. Author SEN designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors HMAS and WAMS managed the analyses of the study. All authors read and approved the final manuscript.

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ABSTRACT

This work demonstrates the successful utilization of the Egyptalum company solid waste (slag) for recovery of high-efficiency γ -alumina to be applied as an effective adsorption medium for nitrate uptake from its aqueous solutions. The composite of the sorbent was characterized by XRD, SEM, FTIR, PZC, and BET surface area (S_{BET}). The new sorbent has high surface area, it was found to be 202.39 m^2/g . Also, the adsorptive capacity for nitrate removal was investigated by a series of batch adsorption experiments, and the influence of the adsorption controlling parameters such as contact time, adsorbent dosage, pH of the solution, initial concentration of nitrates, and temperature on the removal efficiency of NO_3^- by alumina from AISW was evaluated. Furthermore, adsorption isotherms and kinetic studies of the adsorption process were examined. The results of nitrate adsorption were well fitted by pseudo-second order kinetic model, and well explained by Langmuir isotherm model. The maximum adsorption capacity as described from the Langmuir equation was found to be 7.09 mg/g.

*Corresponding author: E-mail: safaa33@yahoo.com;

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1. INTRODUCTION

Recently, a considerable attention has been increasingly devoted towards the industrial operations by-product or the waste of different factories worldwide.

Egyptalum Company in Nag-Hammadi city in upper Egypt produces huge quantities of aluminum solid waste AISW (more than 15000 tons annually)during the production of aluminum metal sheets or during recycling of aluminum metal scraps [1-2]. Due to its highly alkaline nature in water ($\text{pH} > 10.0$) and the presence of different impurities persisting in it, AISW is considered one of the biggest Al waste sources which are difficult to recycle. Herein, accumulation of AISW in these large amounts during aluminum industry creates a serious environmental risk [3], so recovery of useful materials such as active alumina from this aluminum industry chemical waste to be applied in the removal of environmental pollutants is an attractive subject of research for both economic and environmental necessities. In this study, AISW is converted into highly efficient mesoporous $\gamma\text{-Al}_2\text{O}_3$ at low calcination temperature (400°C).

Activated γ -alumina is one of the most important oxidic adsorbents which is widely utilized for water treatment due to its high affinity for a broad range of analytes. γ -alumina exhibit a relatively large number of surface OH groups, which substantially define its adsorption properties. γ -alumina is insoluble in water and can react with both acidic and basic materials due to the amphoteric nature of aluminum oxide. Alumina is characterized by its high specific surface area, mechanical strength, low-temperature modification, very good thermal stability, amphoteric properties, porosity, and ability to be shaped with well-defined pores. Due to these unique properties, porous alumina is typically an excellent candidate as a potential adsorbent in several purification and bleaching processes as well as a catalyst and catalyst support for a large number of industrial processes [4-5].

Nitrates menace all water resources. Contamination of surface and groundwater with nitrates has emerged as an insistent problem on a global scale over the past three decades [5-8]. Elevated nitrate concentrations in potable water supplies can lead to various pernicious health

hazards on both human and animal beings causing in some cases fatal results [4,9-10]. Moreover, the existence of high levels of nitrates in water stimulates numerous environmental risks such as eutrophication [11].

In humankind, Excessive consuming of nitrate-contaminated water can cause many health risks such as methemoglobinemia in newborn infants (also known as a *blue-baby syndrome*) [12-17]. Pregnant women are also insecure from this risk [12,18]. In adults, exposure to high levels of nitrates (above the admissible level) in drinking water is a risk factor for specific cancers due to the formation of carcinogenic N-nitrosamines and N-nitrosamides in the stomach [12]. Recent studies have found that nitrates can cause diabetes [19], the prevalence of infectious diseases, decrease of iodine uptake [20-21], hypertension, abdominal pain, diarrhea, vomiting, blood in urine and stool, changes in the immune system, spontaneous abortions, mental depression, weakness, and birth defects such as central nervous system birth defects [22-24].

In animals, nitrate poisoning causes symptoms like abdominal pain, diarrhea, weight loss, abortion of brood animals, decreased levels of glucose and alkaline phosphatase, dark brown or "chocolate" colored blood in sheep; furthermore, coma and death may happen within a few hours in cattle [4,12] and [25]. For perniciousness of nitrate and the possible health risk, The United States Environmental Protection Agency (USEPA), and Bureau of Indian Standards have set limit of nitrate in drinking water to be 45 mg/L as nitrate (10.2 mg/L nitrate-N) [13], whereas WHO (the World Health Organization) have set international maximum permissible level of 50 mg/L as nitrate (11.3 mg/L nitrate-N) [26].

Due to its high stability and water solubility, nitrate is considered the most common contaminant in groundwater [27]. Towering levels of nitrates have been already observed in groundwater in many parts over the world at alarming rates, including USA, UK, Japan, China, India, Mexico, Morocco, and Saudia Arabia [12, 18,28-30]. Excessive use of fertilizers, municipal wastewater, and septic systems outflow are the main sources of water contamination with nitrates. Additionally, manufacture of explosives, pharmaceutical, nitro-organic compounds, processed meat (nitrates and nitrites are widely

used as meat preservatives), and paper industries [31].

Elimination of nitrate ions from water by the traditional treatment processes is difficult, so numerous methods and techniques have been developed for nitrate removal from waters like, biological denitrification [32-34], reverse osmosis [35], electrodialysis [30], chemical reduction [36-37], ion exchange resins [10,23,38], and adsorption [7,13,27] and [31]. Among these techniques, adsorption provides ease and flexibility in operation, simplicity in design, high efficiency, and many adsorbents can be regenerated for multiple uses by an appropriate desorption process. Therefore, adsorption is considered one of the most efficient methods for removal of pollutants from water [39].

Development of novel and cost-effective adsorbents has increased concern since the production of activated carbon is expensive, non-selective, co-adsorption of naturally occurring organic matter (NOM) can lead to adsorptive interference, and it interacts with treatment chemicals [40], so removal of nitrates onto alumina prepared from AISW is considered a low-cost, economical, efficient and eco-friendly.

2. MATERIALS AND METHODS

2.1 Chemicals

All the chemicals and reagents used in this study were of analytical grade and were used as received without any further purification (except potassium nitrate, which was pre-dried at $\sim 108^\circ\text{C}$ for 24 hours before applying). All experimental solutions were prepared using deionized (DI) water, which was also used to rinse and clean the samples. The stock solution of nitrates was prepared from KNO_3 (1000 mg/L) purchased as an ultrapure product from Merck (Germany), by dissolving 1.63g of KNO_3 (F.W. = 101.1 g/mol.) in 1.0 liter of DI water. Standards and nitrate spiked samples at a required concentration range were prepared by appropriate dilution of stock solution with DI water for further use. New solutions were prepared before each experiment to avoid any possible contamination. The desired pH values of solutions were adjusted by either 0.5 M HCl (37% w/w, F.W. = 36.46 g/mol.) (pure product of Merck) or 0.5 M NaOH (F.W. = 40 g/mol.), which is a 99% pure product of Merck (Germany). Ammonium hydroxide NH_4OH (an AnalaR-grade product of Riedel-de-Haen AG (Germany)) was used for synthesis of adsorbents

(30% w/w, F.W. = 35.04), while NaCl (F.W. = 58.4 g/mol.) was used in the experimental determination of PZC of the tested adsorbents.

2.2 Apparatus

For the characterization of the prepared adsorbents, the surface functional groups were analyzed by Fourier transform infrared spectroscopy (FTIR, the JASCO 4100), the surface area measurements were determined by Automatic ASAP 2010 Micromeritics sorptometer (USA) at liquid nitrogen temperature. The morphology of the synthesized adsorbents was characterized using a scanning electron microscopy (SEM, JSM-5500LV model) operating at 25 kv. In batch experiments, the nitrate concentrations were measured by using Hanna instrument (HI 96786), whereas the pH measurements were made using precision pH-meter (Model PHS-3C). Temperature-controlled water bath with shaker model (WB-110X) was used for shaking the samples at different time intervals.

2.3 Synthesis of Adsorbent

Aluminum solid waste (AISW) was obtained from Egyptalum Company (Nag-Hammadi, Egypt). It's a loose gray powder, crushed and sieved to finer particle size before using. Chemical analysis showed that the AISW has the following composition (in mass %): Al (44.8%), N (6.0%), C (2.0%), Mg (1.5%), Si (1.1%), Fe (1.2%), Na (0.7%), F (0.3%), Ti (0.03%), V (0.02%) and Mn (0.2%). The major constituent compounds of AISW were found to be aluminum oxide, metallic aluminum, fluoride salts and aluminum nitride according to [3]. For the synthesis of the sorbent, 25g of AISW was dissolved in an appropriate volume of hydrochloric acid under vigorous stirring at 60°C . NH_4OH was added dropwisely until the pH of the solution was attained to 8.0. A white precipitate of $\text{Al}(\text{OH})_3$. The final precipitate was washed, dried, and ignited at 400°C in dynamic air. For simplicity, alumina derived from aluminum solid waste was designated as A-AISW.

2.4 Point of Zero Charge (PZC)

Five bottles, each one contains 50 ml of NaCl (0.01M), and 0.1 g of sorbent, were prepared then the starting pH of the solution in each bottle was adjusted by using NaOH (0.5 M) or HCl (0.5 M) solutions at (2, 4, 6, 8, and 10). The final pH of the solutions was measured after 48 hours of

agitation with the sorbent, and ΔpH was calculated according to [41] with some modifications.

For determination of the acidity or basicity of the adsorbent's surface, measurements of the surface pH of the tested adsorbent samples were performed. 0.1 g of dry adsorbent sample was added to 50 ml of distilled water and stirred for 2 hrs. The suspension was kept for 48 hours at the room temperature to reach equilibrium, then the final pH was measured (developed from methodology described by Kyzas et al. [42]).

2.5 Adsorption Studies

Sorption studies were carried out in batch mode owing to its simplicity of reliability and easy to extrapolate at a larger scale for a practical application. A fixed dosage of each sorbent (6.0 g/L) was shaken at 150 rpm with 50 ml of KNO_3 solution at a concentration equals (50 mg/L, $\text{pH} = 6.65 \pm 0.2$) in capped glass bottles (250 ml) at different time intervals to attain the equilibrium at a fixed temperature (except when the effect of temperature is studied). The above samples for each sorbent were filtered off and the nitrate concentration in the supernatant was determined. All the experiments were performed under un-buffered conditions. For accuracy, experiments were performed in duplicate using identical conditions and mean values were taken for calculations (the maximum deviation was 3-5%). All used apparatus in the experiments were thoroughly pre-cleaned with DI water. The percentage of removal of nitrates was calculated by the Eq. (1):

$$\% \text{Removal} = [(C_i - C_f) / C_i] * 100 \quad (1)$$

Where C_i , C_f are the initial and the final concentrations of NO_3^- solution in mg/L. (q_e) is the (mg) amount of the adsorbate per (g) amount of adsorbent (Hafshejani et al., 2016), adsorption capacity (mg/g) was calculated by Eq. (2):

$$q_e = \frac{(C_o - C_e)V}{m \times 1000} \quad (2)$$

Where C_o and C_e are the initial and final concentration at equilibrium (mg/L), m is the mass of adsorbent dose (g), V is the volume of the solution (ml).

2.5.1 pH studies

In order to study the effect of pH of solution on nitrate adsorption onto alumina from AISW, the

pH of KNO_3 solution (50 mg/L) was adjusted to different values (2,3, 4, 6,8, and 10) by using NaOH (0.5 M) or HCl (0.5 M) solutions. The experiments were performed at sorbent dose 6.0 g/L in the batch method, and then samples were shaken for 2 h at the room temperature. The pH of the resulting solutions was then determined.

2.5.2 Adsorbent dosage studies

Different adsorbent doses (from 1 to 20 g/L) were placed in 50 ml of KNO_3 solution at a fixed concentration of (50 mg/L) and at an initial pH value 4.0, then was shaken for 2h at 150 rpm and at the room temperature.

2.5.3 Kinetic studies

For kinetic studies, 50 ml KNO_3 solution (50 mg/L) and fixed adsorbent dose 6.0 g/L were used at different contact time values (35-140 min.) at pH 4.0 at the room temperature.

2.5.4 Effect of initial concentration

50 ml of nitrates at different concentrations (15-85 mg/L) at pH 4.0 was added to sorbent dose 6.0 g/L and shaken for 2h to investigate the effect of Initial concentration on adsorption of nitrates onto alumina prepared from AISW at the room temperature.

2.5.5 Effect of temperature

To evaluate the effect of temperature on sorption of nitrates onto alumina from AISW, 50 ml KNO_3 solution (50 mg/L) and adsorbent dose 6.0 g/L at pH 4.0 were shaken for 2 hr at different temperature intervals (25-55°C).

3. RESULTS AND DISCUSSION

3.1 Characterizations of the Adsorbent

Specific surface area or surface area per unit mass of a solid is an important characteristic in understanding the structure, formation and potential applications of different materials. For this reason, it is necessary to determine and control it accurately. An increase in specific surface area (and therefore increase in the concentration of reactive sites) is expected to lead to an increase in reaction rates or ion sorption at the adsorbent-solution interface. The specific surface area was determined using the theory of Brunauer, Emmet and Teller (BET) applied to the N_2 adsorption/desorption data [43].

The adsorption capacity of active alumina is directly related to its specific surface area and pore volume. In the current study, the surface area of the tested sample (S_{BET} , in $m^2 g^{-1}$) was calculated and derived from nitrogen adsorption isotherms at liquid nitrogen temperature. Obtained results illustrate that A- AISW can be precisely described as mesoporous i.e., containing pores with diameters in the range from 40 to 1000 Å (or 4–100 nm) [3]. The calculated S_{BET} the pore volume, and the average pore diameter were found to be 202.39 m^2/g , 0.39 cm^3/g , and 76.34 Å, respectively. This value exceeds the surface areas of a number of commercially available aluminas as well as aluminas prepared by other researchers such as nano alumina [5] and modified $\gamma-Al_2O_3$ [43].

3.1.1 X-ray diffraction (XRD) analysis

The XRD pattern of calcinated alumina at 400°C in dynamic atmosphere of air is displayed in Fig. 1. The presence of γ -alumina phase in the sample is confirmed.

3.1.2 SEM analysis

The SEM micrographs helped in recognizing the texture and porosity of the A-AISW. Fig. 2 shows the scanning electron microscopy images for the A-ALSW which performed by using SEM & EDX Model FEI INSPECT S50 operating at 20.0 kv Fig. 2. The sponge-like rough surface is observed from the SEM image. This roughness of surface may possibly be useful in nitrate sorption from water. Also, The SEM observations

depicted porous surface texture of the adsorbent material which is needed to be an efficient adsorbent. Rahmani et al. found similar structural features taken by using SEM micrographs for nano alumina [44] and Goli and Upadhyayula also obtained similar texture for chitosan/alumina composite [45]. Roughness and the internal surface of A-AISW are responsible for its high efficiency for nitrate ions removal.

3.1.3 FTIR analysis

The Fourier transform infrared for the solid adsorbent was performed to indicate the functional groups on the sorbent surface responsible for adsorption of nitrates Fig. 3. The FTIR spectra for alumina prepared from AISW were obtained in the range of 600–3500 cm^{-1} . An absorption band at 3470 cm^{-1} was observed, it may be due to deformational vibrations of physically adsorbed water on the surface [9,15]. The absorption band at 2357 cm^{-1} is characteristic for CO_2 [15]. Another band was observed at ca. 1620 cm^{-1} which indicate the presence of alumina, similar results have been reported by [5]. Finally, the absorption band located at ca. 607 cm^{-1} is characteristic to the Al-O vibrations in Al_2O_3 [5].

3.1.4 Point of zero charge PZC and surface properties

Point of zero charge is a pH value exists at which the sum of negative charges equals the sum of positive charges and the net charge of the surface is zero.

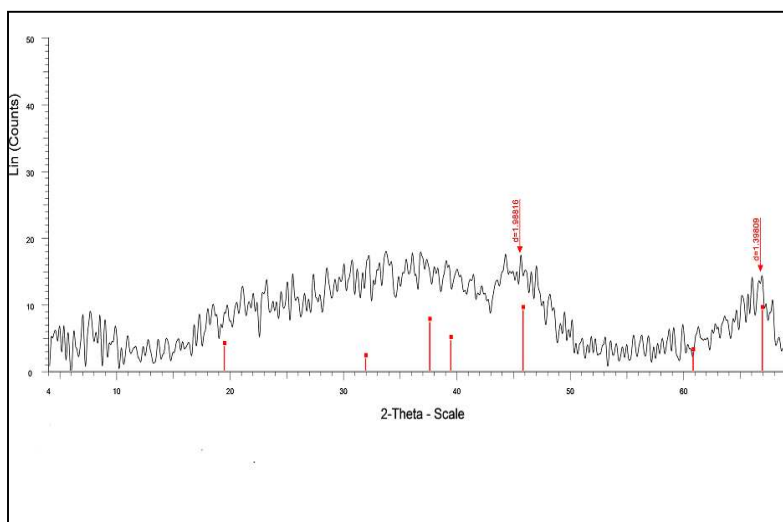


Fig. 1. The XRD pattern for A-AISW

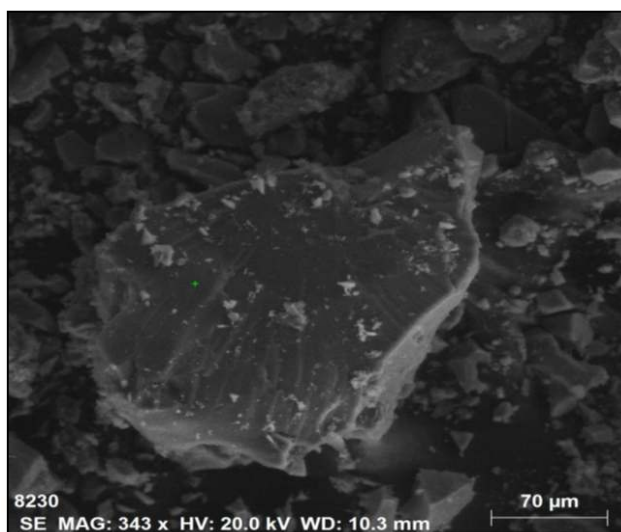


Fig. 2. The SEM micrograph for alumina from AISW

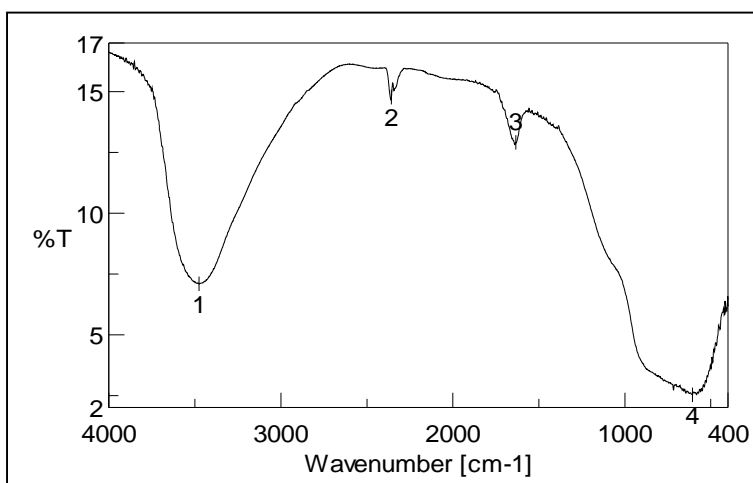
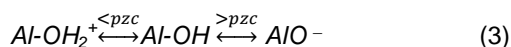


Fig. 3. FTIR Spectra of A-AISW

To assess the affinity of the surface of the sorbent to the ionic species, the position of PZC is essential to be determined [46]. In Fig. 4, the pH-dependent of adsorption process onto alumina from AISW has been demonstrated. The initial pH of the nitrate solution is plotted versus ΔpH (the difference between the initial and final pH values of solutions). The point of intersection of the plot pH initial at $\Delta\text{pH}=0$ is the point of zero charge PZC in which the surface acquires a net zero charge [3]. This is assembled according to Eq. (3):

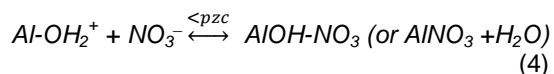


As alumina prepared from AISW is added to a liquid solution below its PZC value ($\text{pH} < 6.2$), the surface of alumina acquires a net positive charge as the surface is protonated via the adsorption of excess hydrogen ions H^+ , whereas, at pH above its PZC value ($\text{pH} > 6.2$), the surface is deprotonated via the desorption process of H^+ , and consequently acquires a net negative charge [47-48]. It means that the surface is positively charged at low pH values and negatively charged at high pH values.

3.2 Effect of pH

The influence of pH values on the adsorption capacity of nitrates onto alumina from AISW has

been illustrated in Fig. 5. The results indicate that the adsorption percentage of nitrates decreases as the initial pH value of the solution increases, similar trends were obtained by [5,47]. Higher adsorption capacities for nitrates were observed at lower pH values (at an acidic medium where $\text{pH} < 6.2$). This may be attributed to the positive surface charges of adsorbent [3,9] according to Eq. (4):



After pH value of 6.2, no significant change in the removal percentage of nitrates with rising pH of the solution. This may be explained by electrostatic repulsion of anionic nitrate by the negatively charged alumina surface at higher pH

(at pH values $> \text{PZC}$) as represented in equation (3). Therefore, we can conclude that the PZC is the key parameter that controls the adsorption uptake of nitrates onto alumina prepared from AISW.

3.3 Effect of Adsorbent Dose

The results constructed in Fig. 6 show an increase in nitrate uptake by increasing the amount of the adsorbent material. The percentage of removal of nitrates increased from 36.5 % to 80.2 % for increasing the sorbent dosage from 1g /L to 20g /L. This may be due to the increase in the active sites on the surface of the adsorbent materials by increasing the dosage. Similar results have been published by [49].

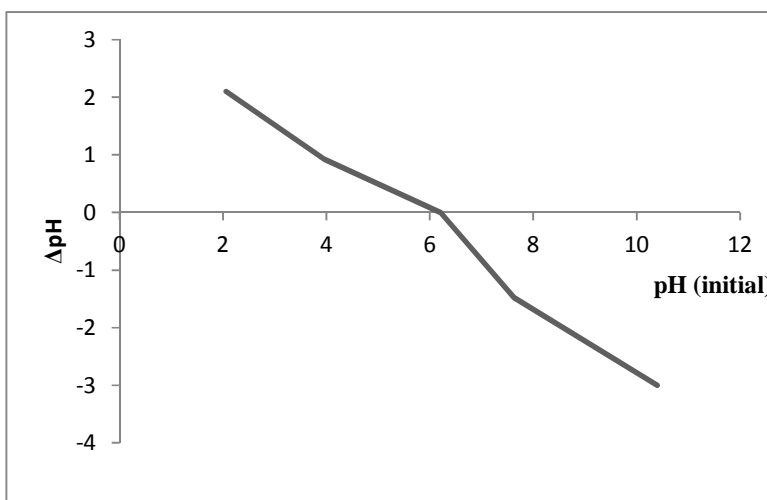


Fig. 4. PZC of A-AISW

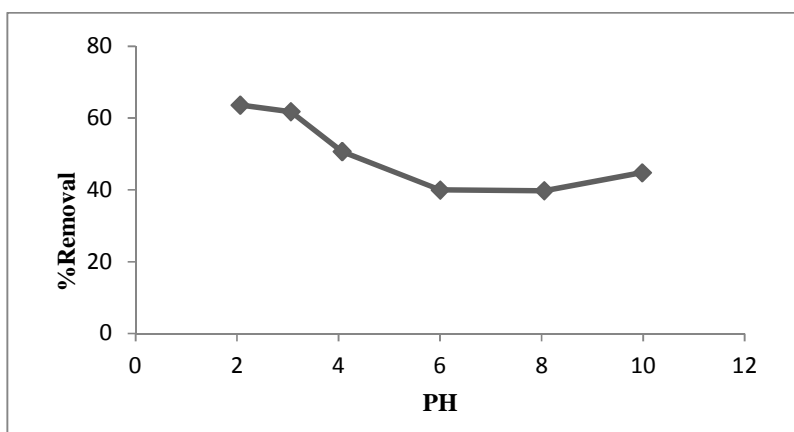


Fig. 5. Effect of pH on percentage removal of nitrate ions by alumina from AISW

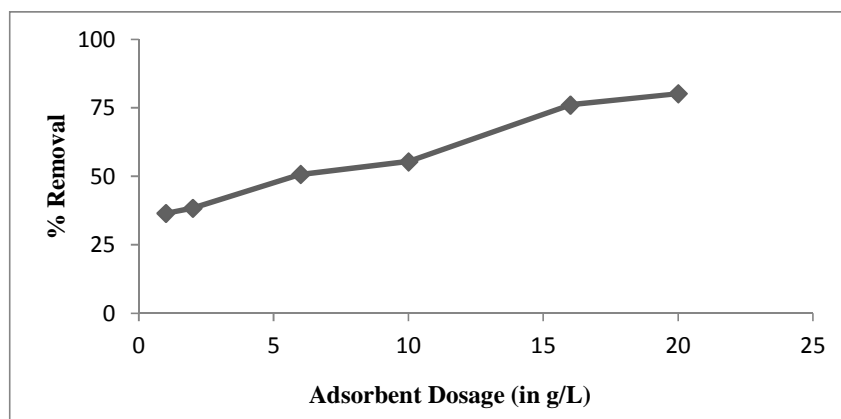


Fig. 6. Effect of sorbent dose on percentage removal of nitrate by A-AISW

3.4 Effect of Initial Nitrate Ions Concentrations

Initial concentrations of nitrate ions play an important role in the mass transfer between the aqueous and solid phase. By increasing initial nitrate concentration, the nitrate removal efficiency decreases. Nitrate removal efficiency decreased from 97.3% to 40.2% for increasing the initial nitrate concentration from 15 mg/L to 85 mg/L at fixed adsorbent doses as plotted in Fig. 7. That is may be attributed to the saturation of the most active sites at a fixed dose of the adsorbent surface with increasing concentration (as more nitrate molecules would be provided). That also may be due to an increased diffusion rate of nitrate to adsorption sites to saturate them; similar trends have been reported by [50].

3.5 Effect of Contact Time

Adsorbent/adsorbate contact time is an important factor in the adsorption processes in contact time depends on the nature of the used system [51]. The influence of time on nitrate uptake by A-AISW is illustrated in Fig. 8. Nitrate removal efficiency increases with increasing the contact time from 0 to 60 minutes. After 60 minutes, the equilibrium is reached. Similar trends have been published by Abderrahim et al. [52].

It's clear from the obtained results that the initial uptake of nitrates onto active alumina prepared from AISW is quite rapid where more than 50% of the nitrate ions are adsorbed within 30 minutes. This fast adsorption though in small time may give a prediction that the type of nitrate adsorption onto alumina prepared from AISW is chemisorption.

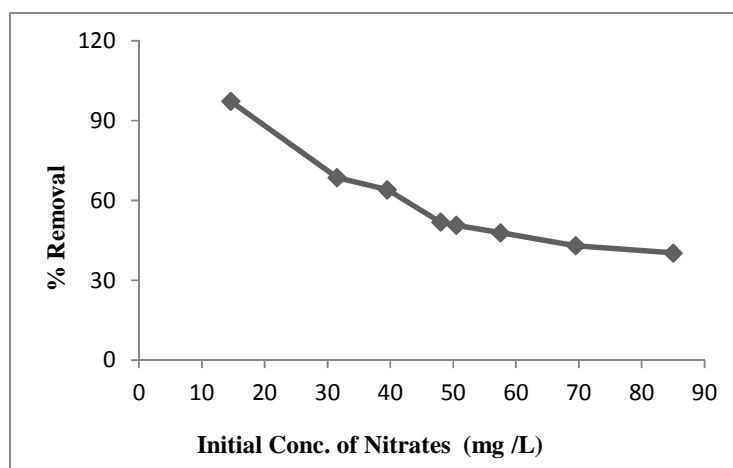


Fig. 7. Effect of initial concentration on percentage removal of nitrate ions by A-AISW

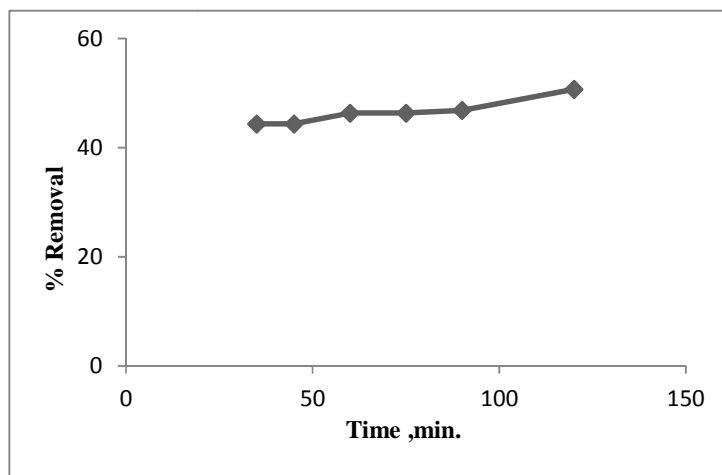


Fig. 8. Effect of contact time on percentage removal of nitrate ions by A-AISW

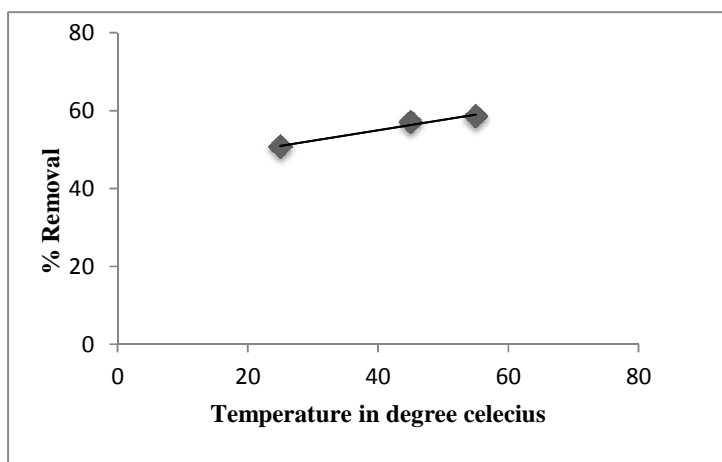


Fig. 9. Effect of temperature on percentage removal of nitrate by A-AISW

3.6 Effect of Temperature

Obtained results in Fig. 9 showed that the percentage of nitrate adsorption increased with the increase of the temperature from 25 to 55°C. That may be attributed to the acceleration of some originally slow adsorption steps and enhancement of the mobility of nitrate ions from the bulk solution towards the adsorbent surface. These results give a proof of the endothermic nature of the adsorption process of nitrates onto active A-AISW. Other authors have similar results [5,47].

3.7 Equilibrium Studies

Analysis of the equilibrium data is important to develop an equation which accurately fit the results and could be used for design

purposes. There are numerous models that can explain the equilibrium studies to describe the relationship between the amount of nitrate ions adsorbed and the nitrate concentration that remaining in the solution of adsorbate (equilibrium adsorption). The equation parameters and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into both the adsorption mechanism and the surface properties and affinity of the sorbent. The most famous models are Langmuir and Freundlich models, which were given by the following equations mentioned below:

3.7.1 Langmuir isotherm model

This model is used to describe the maximum adsorption capacity of the adsorbent

material. The Langmuir isotherm is based on the assumptions that solutes are chemically adsorbed at a fixed number of active sites, and each active site can only hold one molecule (monolayer adsorption). All sites are energetically homogeneous and there is no interaction between the adsorbates. The Langmuir equation is written by Eq. (5):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

And its linear form can be expressed by Eq. (6):

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \cdot \frac{1}{C_e} + \frac{1}{q_m} \quad (6)$$

Where C_e and q_e are as they mentioned above. While q_m (mg/g) is the maximum adsorption capacity and K_L (L/mg) is Langmuir constant related to the affinity of binding sites or bonding energy. An essential feature of Langmuir isotherm is the dimensionless constant separation factor or equilibrium parameter is K_R which can be used to predict whether an adsorption system is favorable or unfavorable [9] can be expressed by Eq. (7):

$$K_R = \frac{1}{1 + K_a C_o} \quad (7)$$

Where K_a is the Langmuir constant and C_o is the initial metal ion concentration.

3.7.2 Freundlich isotherm model

The Freundlich model assumes that the uptake of ions occurs on a heterogeneous surface by reversible and multilayer adsorption. The model can be described by the Eq. (8):

$$q_e = K_f C_e^{\frac{1}{n}} \quad (8)$$

Where K_f (L/g) and n are Freundlich constants characteristics of the system and indicate the adsorption capacity and adsorption intensity, respectively [9]. The linear form of Freundlich equation can be written as Eq. (9):

$$\log q_e = \frac{1}{n} \log C_e + \log K_f \quad (9)$$

3.7.3 Temkin isotherm model

The Temkin isotherm is usually used for heterogeneous surface energy systems (non-uniform distribution of sorption heat) [53]. The Temkin equation suggests a linear decrease of adsorption energy as the degree of completion of

the adsorptional centers of an adsorbent is increased. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbent-adsorbate interactions. As mentioned before, the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [20]. The Temkin isotherm can be expressed in a linear form as presented in equation (10):

$$q_e = B \ln A + B \ln C_e \quad (10)$$

Where $B = RT/b$, B is a constant related to the heat of sorption (J/mol.) obtained from the Temkin plot (q_e versus $\ln C_e$). A is the equilibrium binding constant (L/mg), R is the universal gas constant (J.mol⁻¹.K⁻¹), T is temperature K, and b is the heat of adsorption which is directly related to coverage of nitrate ions onto A-AISW due to adsorbent-adsorbate interaction. At temperature =298K, the b value ($b = RT/B$) nitrate adsorption onto A-AISW is higher than 80 KJ/mol. ($b = 1698.13$ KJ/mol) Which indicating a chemical adsorption process and is a quite higher that reveals the strong ionic interaction between nitrate ions and A-AISW [53].

The Freundlich, Langmuir, and Temkin plots are presented in (Figs. 10, 11 and 12) and their constants were calculated and presented in Tables 1, 2.

The parameter K_R derived from Langmuir equation indicates the shape of isotherm where K_R can take so many values. Such values are $0 < K_R < 1$; $K_R > 1$; $K_R = 1$ or $K_R = 0$ which denotes to favorable, unfavorable, linear or non-linear adsorption process, respectively [47].

The values of correlation coefficients (R^2) of both Langmuir and Freundlich equations are higher than 0.94 which imply that both monolayer adsorption and heterogeneous surface conditions are possible. Also of note, that the R^2 values of two models were very close to one another, that indicate the adsorption of nitrate on A-AISW is complex and may be controlled by multiple processes.

The values of constants for each adsorption isotherm model were calculated to evaluate the surface properties and affinity limit of the adsorbent material for nitrate ions. The obtained results were summarized in Table 1. All the obtained results of the equilibrium study suggest

that A-AISW is an effective adsorbent for the nitrate adsorption from aqueous solution, where (i) the values of the Freundlich isotherm constants (K_f and n) showed easy uptake and good adsorption process of nitrate ions from aqueous solutions with high adsorptive capacity. Where, the value obtained from Freundlich isotherm constant n is 5.68 ($n > 1$), gives an indication that the removal of nitrate ions onto A-

AISW is an effective adsorption process. Also, the high value of K_f indicates the high adsorption efficiency for nitrates by A-AISW. (ii) According to the results shown in Table 2, all the K_R values between 0 and 1 (range between 0.275 and 0.662) that indicate a favorable and efficient adsorption process in the entire initial concentration and signifies that A-AISW is a proper adsorbent for nitrate ions adsorption.

Table 1. Freundlich, langmuir, and temkin constants for A-AISW at 25± 2°C

Freundlich constants				Langmuir constants			Temkin constants		
n	1/n	K_f	R^2	q_m	K_L	R^2	B	A	R^2
5.68	0.176	1.522	0.946	7.092	0.034	0.985	1.46	0.089	0.858

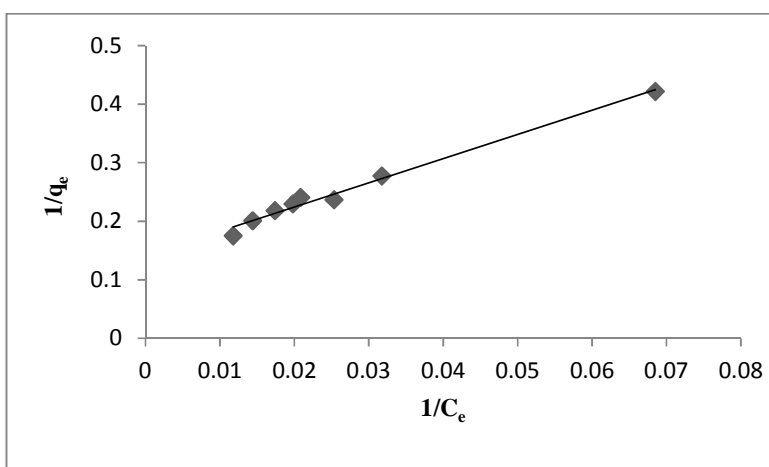


Fig. 10. Langmuir adsorption isotherm, $1/C_e$ versus $1/q_e$ for A- AISW

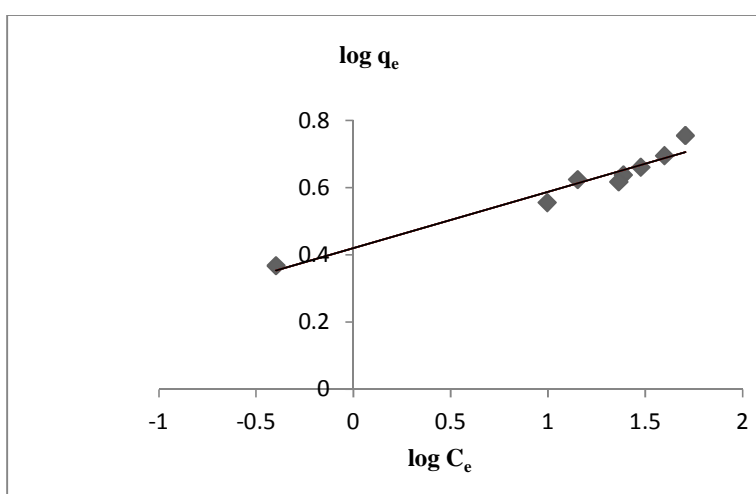


Fig. 11. Freundlich adsorption isotherm, $\log C_e$ versus $\log q_e$ for A- AISW

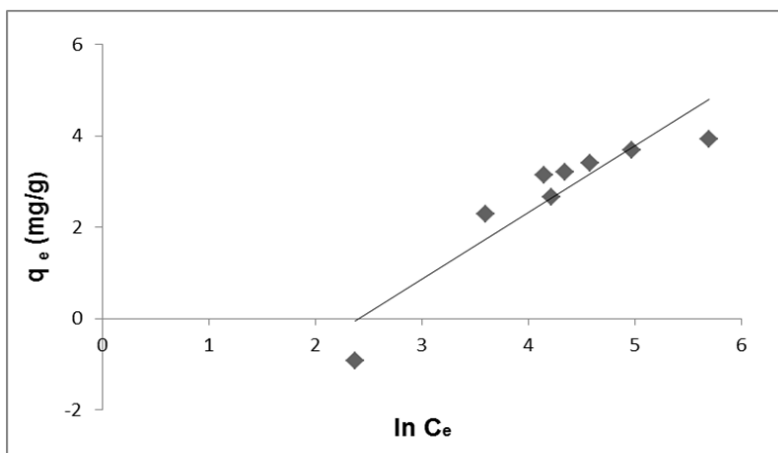


Fig. 12. Temkin plot for nitrate ions-(A-AISW) system at room temperature

Table 2. Langmuir dimensionless equilibrium parameter for A-AISW at 25 ± 2°C

Initial concentration (mg/L)	K _R values
15	0.662
30	0.494
40	0.423
50	0.370
60	0.328
70	0.295
85	0.257

3.8 Kinetic Studies

The adsorption kinetics deal with the rate at which sorption occurs. The order of adsorbate-adsorbent interactions has been described by using various kinetic models. Of these, pseudo-first order, pseudo-second order, and intra-particle diffusion models are used. The equation parameters of these models often provide some insight into both adsorption mechanism and the affinity of the sorbent.

3.8.1 Pseudo-first order model

The Lagergren first-order equation describes the adsorption of liquid–solid systems based on the solid capacity [54]. The linear form of Lagergren is written as in Eq. (11):

$$\log(q_e - qt) = \log q_e - \frac{K_1}{2.303} t \quad (11)$$

Where the q_e and q_t (mg/g) are the amounts of adsorbate per amount of adsorbent at equilibrium and at any time t and K_1 (min^{-1}) is the rate constant of pseudo-first order.

3.8.2 Pseudo-second order model

Pseudo-second order equation indicates the sorption system of nitrates [55] and can be expressed as Eq. (12):

$$\frac{t}{qt} = \frac{1}{h} + \frac{1}{q_e} t \quad (12)$$

Where $h = k_2 q_e^2$

K_2 (g /mg. min.) is the rate constant of pseudo-second order model.

3.8.3 Intra-particle diffusion model

Beside the adsorption on the outer surface of adsorbent, there is a possibility of transport of adsorbate ions from the solution to the pores of adsorbent due to stirring in a batch process. This possibility was tested in order to show the existence of intra-particle diffusion in the adsorption process, (q_t). The most-widely applied intra-particle diffusion equation expressed by Weber and Morris equation, the amount of nitrate ions sorbed per unit mass of sorbent at time t was plotted as a function of square root of time ($t^{0.5}$) [56,57].

The intra-particle diffusion model equation is written by Eq. (13):

$$qt = K_{ad} t^{0.5} \quad (13)$$

k_{ad} is the intra-particle diffusion rate constant ($\text{mg/g min}^{0.5}$).

The plots of pseudo-first order, pseudo-second order, and intra-particle diffusion model are

presented in Figs. 13, 14 and 15, while their constants are shown in Table 3.

Kinetics data for nitrate ions adsorption by A-AISW at fixed temperature were tabulated in Table 3, while the values of the respective correlation coefficient of applicability (R^2) as well as the constants of pseudo-first, pseudo-second, and intra-particle diffusion model for nitrate-(A-AISW) system were summarized in Table 3. According to the correlation factors R^2 values, the obtained results are fitted well only the pseudo-second order model, furthermore the experimental value of the equilibrium uptake $q_e(\text{exp.})$ of nitrate adsorption by A-AISW (5.01 mg/g) is closer to the calculated value $q_e(\text{cal.})$ of the pseudo-second order model (4.17 mg/g). This result gives a sign that nitrate uptake onto

A-AISW is controlled by chemical reaction. Similar results have been obtained by other authors [55]. Also, Equation (14) is used to determine the best-fit for kinetic models by the square sum of errors (SSE) values [53]:

$$SSE = \sum \frac{(q_e(\text{exp}) - q_e(\text{cal}))^2}{q_e(\text{exp})} \quad (14)$$

The lowest value of SSE is the best model for the particular system. It is clear from SSE that pseudo-second order kinetic (SSE = 0.0179) has lower SSE value than pseudo-first-order kinetic (SSE = 2.654) which prove that the experimental data follow pseudo-second-order kinetics comparatively better than pseudo-first-order.

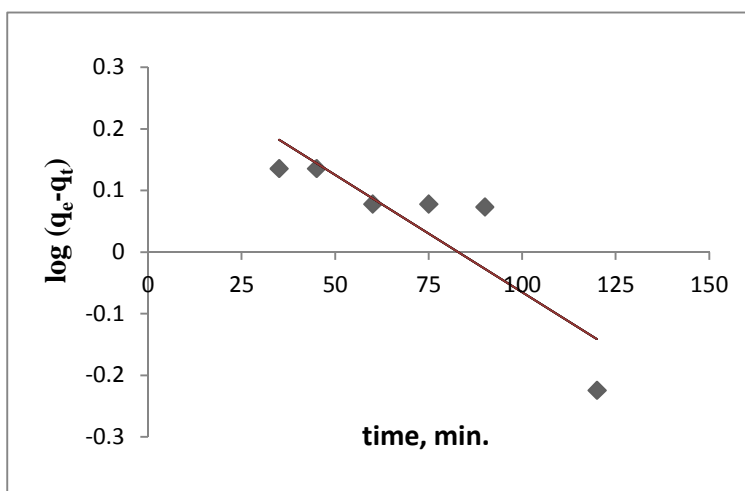


Fig. 13. Linear plots of Lagergren rate equation for nitrate removal by alumina from AISW

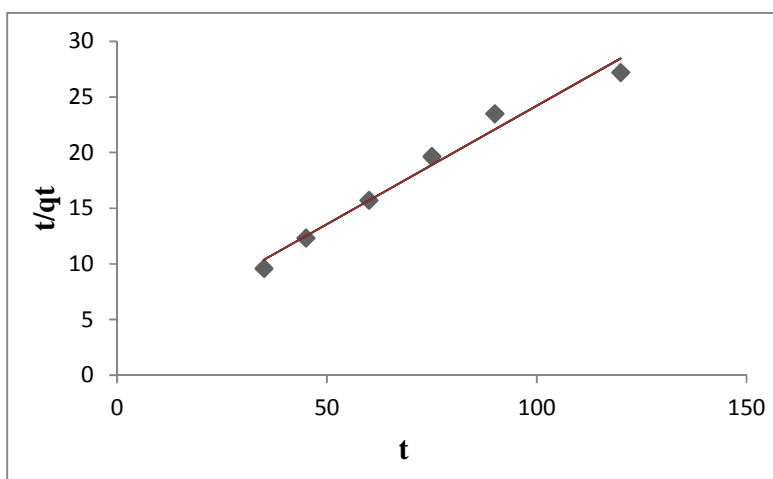


Fig. 14. Linear plots of pseudo-second order for nitrate removal by alumina from AISW

Table 3. Pseudo–first, pseudo–second, and intraparticle diffusion model constants for A-AISW

Pseudo-first order			Pseudo-second order			Intra-particle diffusion		q _e (Exp)
K ₁	q _e	R ²	K ₂	q _e	R ²	K _{ad}	R ²	
6.91×10 ⁻³	1.37	0.765	1.54×10 ⁻²	4.72	0.978	0.135	0.761	5.02

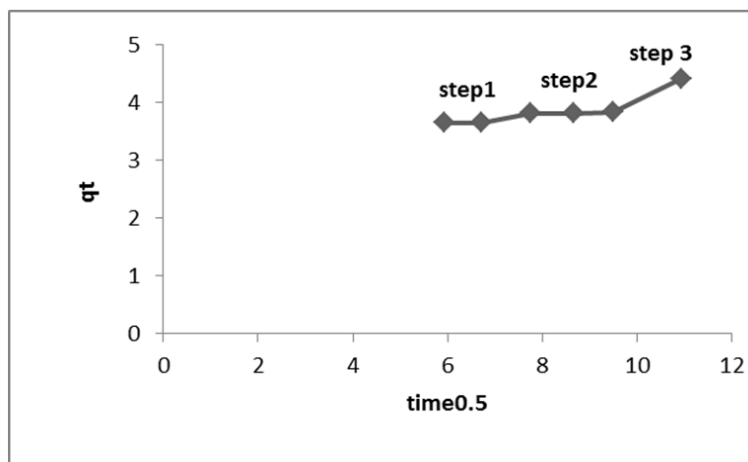


Fig. 15. Linear plots of Weber and Morris Intraparticle diffusion, q_t versus $t^{0.5}$ for removal of nitrates by alumina from AISW

In this work, the intra-particle particle diffusion model linear plot as shown in Fig. 15. The curvedoes not pass through the origin. This indicates that the removal of nitrate ions is complex and the intra-particle diffusion is not the only rate-limiting step for the whole reaction [20, 56]. The overall rate of adsorption process of nitrate by intra-particle diffusion model can be given by the following three steps: (1) the first step represents the diffusion of nitrate ions to the external surface of the sorbent (fluid transport), (2) the second step indicates the gradual adsorption (film diffusion), (3) the third step explains the final equilibrium due to reduction of nitrate concentration in the solution and decrease of active sites of alumina prepared from AISW (surface diffusion) [47].

4. CONCLUSION

Batch experimental tests on nitrate adsorption showed that alumina prepared from AISW has a high affinity for adsorbing nitrate pollution. The results of this study showed that the rate of adsorption of nitrates obeys pseudo–second order rate equation. The obtained results are best fitted to Langmuir and Freundlich adsorption isotherms. All the equilibrium and kinetic studies prove that adsorption of nitrates onto alumina prepared from AISW is chemisorption. At the end of this study, we can suggest using alumina

prepared from AISW for removal of nitrates with high capacity in a short time and considered as a low –cost, efficient and environmental –friendly adsorbent material.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

- Mohamed MA, Kassim ME, El-Katatny EA. Optimization of the Extraction of Aluminum Sulphate and Ammonium Aluminum Sulfate Alum from Aluminum Dross Tailings. Mater. Res. 1998;13(4):1075-1083. DOI: 10.1557/JMR.1998.0149
- El-Katatny EA, Halawy SA, Mohamed MA, Zaki MI. Recovery of high surface area alumina from aluminum dross tailings. Chem. Tech. Biotech. 2000;75:394-402.
- El-Katatny EA, Halawy SA, Mohamed MA, Zaki MI. Surface composition, charge and texture of active alumina powders recovered from aluminum dross tailings chemical waste. Powder Tech. 2003;132: 137–144. DOI: 10.1016/S0032-5910(03)00047-0

4. Ahmad HB, Abbas Y, Hussain M, Akhtar N, Ansari TM, Zuber M, Zia KM, Arain SA. Synthesis and application of alumina supported nano zero valent zinc as adsorbent for the removal of arsenic and nitrate. *Korean J. Chem. Eng.* 2014;31(2): 284-288.
DOI: 10.1007/s11814-013-0219-0
5. Bhatnagar A, Kumar E, Sillanpaa M. Nitrate removal from water by nano-alumina: Characterization and sorption Studies. *Chem. Eng.* 2010;163:317–323.
DOI: 10.1016/j.cej.2010.08.008
6. Hao Z, Xu X, Jin J, He P, Liu Y, Wang D. Simultaneous removal of nitrate and heavy metals by iron metal. *Zhejiang Univ. Sci.* 2005;6(5):307-310.
DOI: 10.1631/jzus.2005.B0307
7. Traistaru GA, Covaliu CI, Gallois GP, Cursaru DL, Jitaru I. Removal of nitrate from water by two types of sorbents, characterization and sorption studies. *Rev. Chem. (Bucharest)*. 2012;63(3):268-271.
8. Halajnia A, Oustan S, Najafi N, Khataee AR, Lakzian A. Adsorption–desorption characteristics of nitrate, phosphate, and sulfate on Mg–Al layered double hydroxide. *Appl. Clay Sci.* 2013;80-81: 305–312.
Available: <http://dx.doi.org/10.1016/j.clay.2013.05.002>
9. Faye G, Bekele W, Fernandez N. Removal of nitrate ion from aqueous solution by modified Ethiopian bentonite Clay. *Inter. J. of Res. in Pharm. and Chem.* 2014;4(1): 192-201.
10. Gutsanu V, Bulicanu V. Removal of nitrate/nitrite ions by modified with metal-containing compounds strongly basic exchanger using response surface methodology. *Ion Exchange Letters.* 2014; 7:1-5.
11. Öztürk N, Bektas TE. Nitrate removal from aqueous solution by adsorption onto various materials. *Hazard. Mater.* 2004;112:155–162.
DOI: 10.1016/j.jhazmat.2004.05.001
12. Shrimali M, Singh KP. New methods of nitrate removal from water. *Environ. Pollut.* 2001;112:351-359.
13. Namasivayam C, Sngeetha D. Removal and recovery of nitrate from water by ZnCl₂ activated carbon from coconut coir pith, an agricultural solid waste. *Indian. J. of Chem. Tech.* 2005;12:513-521.
DOI: 10.1016/j.chemosphere.2005.02.051
14. Ayyasamy PM, Shanthy K, Lakshmanaperumalsamy P, Lee S, Choi N, Kim D. Two-stage removal of nitrate from groundwater using biological and chemical treatments. *Biosci. and Bioeng.* 2007;104(2):129-134.
DOI: 10.1263/jbb.104.129
15. Islam M, Patel R. Physicochemical characterization and adsorption behavior of Ca/Al chloride hydrotalcite-like compound towards removal of nitrate. *Hazard. Mater.* 2011;190:659–668.
DOI: 10.1016/j.jhazmat.2011.03.094
16. Bhatnagar A, Sillanpaa M. A review of emerging adsorbents for nitrate removal from water. *Chem. Eng. J.* 2011;168:493-504.
DOI: 10.1016/j.cej.2011.01.103
17. Dioum A, Hamoudi S. Mono- and quaternary-ammonium functionalized mesoporous silica materials for nitrate adsorptive removal from water and wastewaters. *Porous Mater.* 2014;21:685–690.
DOI: 10.1007/s10934-014-9815-6
18. Galaviz-Villa I, Landeros-Sánchez C, Castañeda-Chávez MR, Martínez-Dávila JP, Pérez-Vázquez A, Nikolskii-Gavrilov I, Lango-Reynoso F. Agricultural contamination of subterranean water with nitrates and nitrites: an environmental and public health problem. *J. of Agricultural Sci.* 2010;2(2):17-30.
DOI: 10.5539/jas.v2n2p17
19. Khan MA, Ahn Y, Kumar M, Lee W, Min B, Kim G, Cho D, Bae Park W, Jeon B. Adsorption studies for the removal of nitrate using modified lignite granular activated carbon. *Separation Sci. and Tech.* 2011;46(16):2575-2584.
DOI: 10.1080/01496395.2011.601782
20. Demiral H, Gunduzoglu G. Removal of nitrate from aqueous solutions by activated carbon prepared from sugar beet bagasse. *Bioresource Technol.* 2010;101:1675–1680.
DOI: 10.1016/j.biortech.2009.09.087
21. Brekke C. Sorption of nitrates to activated carbon. MSc Thesis. Faculty of science and technology, Stavanger University; 2012.
22. Lohumi N, Gosain S, Jain A, Gupta VK, Verma KK. Determination of nitrate in environmental water samples by conversion into nitrophenols and solid phase extraction–spectrophotometry, liquid chromatography or gas chromatography-

- mass spectrometry. *Analytica Chimica Acta*. 2004;505(2):231-237.
Available:<https://doi.org/10.1016/j.aca.2003.10.060>
23. Samatya S, Kabay N, Yuksel U, Arda M, Yuksel M. Removal of nitrate from aqueous solution by nitrate selective ion exchange resins. *Reactive & Functional Polymers*. 2006;66:1206–1214.
DOI:10.1016/j.reactfunctpolym.2006.03.009
 24. Batheja K, Sinha AK, Seth G. Studies on water treatment for removal of nitrate. *Asian J. of Exp. Sci*. 2009;23(1):61-66.
 25. Yakout SM, Mostafa AA. Equilibrium isotherm studies for removal nitrate from aqueous solutions as hazardous anion in animal system. *Animal and Veter. Adv*. 2014;13(12):728-731.
 26. WHO (World Health Organization), *Guidelines for Drinking Water Quality*, World Health Organization, Geneva; 1993.
 27. Aroke UO, Ibrahim M, Okoroma LA. Parametric studies of nitrate ion sorption on varied mass of HDTMA-Br modified kaolinite clay. *Inter. J. of Emerg. Tech. and Adv. Eng*. 2015;5(3):14-23.
 28. El-Garawany MM, Al-Eed MA, Assubaie FN. Determination of nitrate and nitrite levels in soil and groundwater in Al Hassa area, Saudi Arabia. *Scientific J. of King Faisal Univ. (Basic and Appl. Sci.)*. 2005; 6(2):87-97.
 29. Sahli MAM, Annouarb S, Mountadarb M, Soufianec A, Elmidaoui A. Nitrate removal of Brackish underground water by chemical adsorption and by electrodialysis. *Desalination*. 2008;227:327–333.
DOI: 10.1016/j.desal.2007.07.021
 30. Ayyasamy PM, Rajakumar S, Sathishkumar M, Swaminathan K, Shanthi K, Lakshmanaperumalsamy P, Lee S. Nitrate removal from synthetic medium and groundwater with aquatic macrophytes. *Desalination*. 2009;242:286-296.
DOI: 10.1016/j.desal.2008.05.008
 31. Mohsenipour M, Shahid S, Ebrahimi K. Nitrate adsorption on Clay Kaolin: Batch tests. *Chem*. 2015;1-7.
Available:<http://dx.doi.org/10.1155/2015/397069>
 32. Gómez MA, González-López J, Hontoria-Garc E. Influence of carbon source on nitrate removal of contaminated groundwater in a denitrifying submerged filter. *Hazard. Mater*. 2000;80:69–80.
DOI: 10.1016/S0304-3894(00)00282-X.
 33. Ovez B, Margaeret J, Saglam M. Biological denitrification in drinking water treatment using the seaweed *Gracilaria verrucosa* as carbon source and biofilm carrier. *Water Environ. Res*. 2006;78(4):430-434.
DOI: 10.2175/106143006X9882
 34. Foglar L, Babić A, Šiljeg M. The use of bacteria attached to Lewatit M600 for denitrification of the Cetina surface water. *WSEAS Transactions of Environ. and Develop*. 2010;6(2):113-122.
 35. Schoeman JJ, Steyn A. Nitrate removal with reverse osmosis in a rural area in South Africa. *Desalination*. 2003;155:15-26.
 36. Li T, Li S, Wang S, An Y, Jin Z. Preparation of nanoiron by water-in-oil (W/O) microemulsion for reduction of nitrate in groundwater. *Water Resource and Protection*. 2009;1:1-57.
 37. Comba S, Martin M, Marchisio D, Sethi R, Barberis E. Reduction of nitrate and ammonium adsorption using microscale iron particles and zeolite. *Water Air Soil Pollut*. 2012;223:1079–1089.
DOI: 10.1007/s11270-011-0926-2
 38. Chabani M, Amrane A, Bensmaili A. Kinetics of nitrates adsorption on Amberlite IRA 400 resin. *Desalination*. 2007;206: 560-567.
DOI: 10.1016/j.desal.2006.04.064
 39. Huo L, Yang Q, Shang H. Kinetics and thermodynamics study of nitrate adsorption on granular ferric hydroxide. *Fresenius Environ. Bulletin*. 2012; 21(3a):789-796.
 40. Aroke UO, El-Nafaty UA, Osha OA. Removal of oxyanion contaminants from wastewater by sorption onto HDTMA-Br surface modified organo-kaolinite clay. *Inter. J. of Emerg. Tech. and Adv. Eng*. 2014;4(1):475-484.
 41. Lopez-Ramon MV, Stoeckli F, Moreno-Castilla C, Carrasco-Marin F. On the characterization of acidic and basic surface sites on carbons by various techniques. *Carbon*. 1999;37:1215-1221.
 42. Kyzas GZ, Deliyanni EA, Matis KA. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* Activated carbons produced by pyrolysis of waste potato peels: Cobalt ions removal by adsorption. 2016;490:74–83.
 43. Afkhami A, Bagheri H, Madrakian T. Alumina nanoparticles grafted with functional groups as a new adsorbent in efficient removal of formaldehyde from

- water samples. Desalination. 2011;281: 151–158.
DOI: 10.1016/j.desal.2011.07.052
44. Rehman R, Mahmud T, Anwar J, Salman M, Shafique U, Zaman WU, Ali F. Removal of Alizarin Red S (Dye) from Aqueous Media by Using Alumina As An Adsorbent". J. Chem. Soc. Pak. 2011; 33(2):228-232.
45. Golie WM, Upadhyayula S. Continuous Fixed-Bed Column Study for The Removal of Nitrate from Water Using Chitosan/Alumina Composite. Water Process Eng. 2016;12:58–65.
DOI: 10.1016/j.jwpe.2016.06.007
46. Kosmulski M. The pH-dependent surface charging and the points of zero charge. Colloid and Interface Sci. 2002;253:77–87.
47. Hafshejani LD, Hooshmand A, Nasri AA, Mohammadi AS, Abbasi F, Bhatnagar A. Removal of nitrate from aqueous solution by modified sugarcane bagasse biochar. Ecol. Eng. 2016;95:101–111.
Doi: 10.1016/j.ecoleng.2016.06.035
48. Park J, Regalbuto JR. A simple, accurate determination of oxide PZC and strong buffering effect of oxide surfaces at incipient wetness. Colloid and Interface Sci. 1995;175:239-252.
49. Mise SR, Bassetty R. Study of nitrate adsorption characteristics on Red soil. Inter. J. of Res. in Eng. and Tech. 2013; 334-337.
50. Harmayani KD, Anwar AHMF. Adsorption of nutrients from storm water using sawdust. Inter. J. of Environ. Sci. and Develop. 2012;3(2):114-117.
51. Parab H, Joshi S, Shenoy N, Lali A, Sarma US, Sudersanan M. Determination of Kinetic and Equilibrium Parameters of The Batch Adsorption of Co(II), Cr(III) and Ni(II) onto Coir Pith. Process Biochem. 2006;41: 609-615.
DOI: 10.1016/j.procbio.2005.08.006
52. Abderrahim O, Ferrah N, Didi MA, Villemin D. A new sorbent for europium nitrate extraction: phosphonic acid grafted on polystyrene resin. Radioanal Nucl. Chem. 2011;290:267-275.
DOI: 10.1007/s10967-011-1243-3
53. Erhayem M, Al-Tohami F, Mohamed R, Ahmida K. Isotherm, Kinetic, and Thermodynamic Studies for The Sorption of Mercury (II) onto Activated Carbon from Rosmarinus Officinalis Leaves. American J. of Analytical Chem. 2015;6:1-10.
DOI: 10.4236/ajac.2015.61001
54. Ho Y. Citation review of Lagergren kinetic rate equation on adsorption reaction. Scientometrics. 2004;59(1):171-177.
55. Chatterjee S, Woo SH. The removal of nitrate from aqueous solutions by chitosan hydrogel beads. Hazard. Mater. 2009;164: 1012–1018.
56. Singh T, Pant K. Equilibrium, kinetics and thermodynamic studies for adsorption of As (III) on activated alumina". Separation and Purification Technol. 2004;36:139-147.
57. Mishra PC, Patel RK. Use of agricultural waste for the removal of nitrate-nitrogen from the aqueous medium. Environ. Manage. 2009;90:519-522.
DOI: 10.1016/j.jenvman.2007.12.003

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