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Testing and Evaluation Performance of Borosilicate Glasses for Ammonia, Nitrate, and Total Nitrogen Removal from Industrial Wastewater

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Abstracts: Several studies were conducted utilizing various adsorbents in an effort to remove NH_3^+, NO_3, and total nitrogen (TN) by adsorption process. In this study, Borosilicate glass is used as an adsorbent material. The effectiveness of the adsorbent in removing NH_3^+, NO_3, and TN was examined, that in relation to the effect of solution characteristics. Three different types of glass intermediate oxides (Al_2O_3, SnO, and Bi_2O_3) were used to synthesize three different samples of borosilicate glass (adsorbents), that to study their effect on the adsorption efficiency of borosilicate glass. Aluminum oxide Al_2O_3 was used to synthesize adsorbent (I), tin oxide SnO was used to synthesize adsorbent (J), and bismuth oxide Bi_2O_3 was used to synthesize adsorbent (K). Adsorbents (I, J, and K) achieved a clear improvement in the performance of the adsorption process. Despite the convergence of competencies, adsorbents J and K were superior to adsorbent I. With adsorbent K and an initial concentration of contaminants 28 mg NH_3^+/ L, 28 mg NO_3/ L, and 60 mg TN / L, the removal efficiency of NH_3^+, NO_3, and TN was 49.5%, 55%, and 40%, respectively. The removal efficiency increased with initial concentration of contaminants increasing, which became around 79% NH_3^+, 93% NO_3, and 88% TN for adsorbent K. The best efficiency of ammonia removal achieved with pH value 8.9, it was 64.1%, 75.3%, and 77.1% for adsorbents I, J, and K, respectively. The highest efficiency of nitrate removal was in acidic case, reaching 90.1%, 95.2%, and 93.8% for adsorbents I, J, and K, respectively, at pH value 4.1. Adsorption data were fitted with Langmuir and Freundlich isotherm models to demonstrate the adsorption behavior of NH_3^+, NO_3, and TN onto adsorbents (I, J, and K). It was found that the data were well fitted to both models. Overall, the findings demonstrated that borosilicate glass has the potential to be an effective adsorbent for the removal of ammonia, nitrate, and total nitrogen from industrial effluent.

Keywords: Ammonia, Nitrate, Total Nitrogen, Borosilicate Glass, Adsorption.

1. INTRODUCTION

One of the biggest problems of this century in numerous countries is water scarcity, as it has become a global problem and it is believed that water will be the scarcest resource in the future. Therefore, searching for the causes of water contamination and attempting to treat them must be a priority. Water contamination appears to be mostly caused by anthropogenic activities, such as commercial, industrial, and municipal operations. Because ammonia is used in industries including agriculture fertilizers, plastic manufacture, and explosives, it was frequently detected in industrial effluent [1], [2]. Ammonia and nitrogen derivatives are typically present in wastewater from factories, agricultural drainage systems, and houses. As reported in a previous study, the Haber-Bosch process, which creates ammonia by combining molecular hydrogen and nitrogen, generates almost 2×10^{11} kg of ammonia annually throughout the world [3]. Most is used for fertilizer and agriculture while the remaining is used for other purposes including industrial processes and explosives [3], [4]. 40–50% of the total nitrogen (TN) in wastewater is converted to ammonia [5], [6]. Since there is too much ammonia in water streams, there is significant global pollution of drinking water. These pollutants are hazardous to humans and exist in drinking water [7]–[9]. Therefore, it was important to develop new, cost-effective techniques for eliminating ammonia and other contaminants from the water. Indeed, a lot of researchers have started looking into and working on removing contaminants like ammonia and many others in the past. The use of conventional techniques to remove ammonia has a number of limitations [10]. As a result, a variety of techniques, including biological nitrification, air-stripping, ion exchange, and adsorption, were used to remove ammonia. In order to remove ammonia, the biological nitrification-denitrification process is frequently utilized [11]. However, as industrial effluent contains a considerable amount of ammonia, such a procedure is inappropriate for it [12], [13]. When ammonia levels are high, alternative techniques are appropriate [14], such as precipitation [15], air-stripping [16]–[18],breakpoint chlorination [19], ion exchange [20], [21], and adsorption [22]–[24]. Adsorption is a surface phenomenon that works as adsorbent particles increase by contaminants adhering to the adsorbent particles' surface. Adsorption technique is thought to be useful for the removal of contaminants since it is simple and conventional [25]. Adsorbents' function is the attraction of contaminants molecules to stick to their atoms [26]. Researchers in the fields of chemistry and engineering studied the usage of activated carbon as an adsorbent and worked to improve it [27]. For instance, zeolite was employed as an adsorbent to remove ammonia [28], [29]. Bentonite was utilized as an adsorbent in other tests, which produced reliable findings [30]–[33]. It is important to remember that natural minerals can be expensive and susceptible to scarcity. Additionally, artificial minerals must be produced under challenging conditions, making an adsorbent media necessary. Researchers employed the metakaolin geopolymer MK-GP as an adsorbent for ammonia removal [34]–[37]. In the present study, a new adsorbent (borosilicate glass) was synthesized to reduce ammonia (NH_3^+), nitrate (NO_3), and total nitrogen (TN) from industrial wastewater. Borosilicate glass is one of the oxide glasses types, as the oxide glasses are characterized by the presence of dangling bonds, in addition to the surface area containing active sites. These factors make borosilicate glass a suitable material for use as an adsorbent, where contaminants molecules are attracted to its surface occupy its active sites or to form bonds. Borosilicate glass contains in its chemical composition an intermediate oxide, the used intermediate oxides for this study were aluminum oxide Al_2O_3, tin oxide SnO, and bismuth oxide Bi_2O_3. Aluminum oxide was used in the chemical composition of adsorbent (I), tin oxide was used in the chemical composition of adsorbent (J), and bismuth oxide was used in the chemical composition of adsorbent (K). The aim of this work is studying the efficiency of borosilicate glasses in NH_3^+, NO_3, and TN removal, with using different types of intermediate oxide, and monitoring the effect of solution characteristics on the adsorption efficiency.

2. MATERIEL AND METHODS

2.1. Chemicals

The analytical-grade chemicals that were utilized were all bought from Alfa Aesar: Boron oxide B_2O_3 with purity 98%, Silicon Oxide (SiO_2) with purity 99.5%, Copper (II) Oxide (CuO) with purity 99%, Aluminum Oxide (AL_2O_3) with purity 99.5%, Bismuth oxide (Bi_2O_3) with purity 99%, and Tin (II) oxide (SnO) with purity 99%. Sodium carbonate (Na_2CO_3) was purchased from Merck Company; its purity was 99.8%.

2.2. Solution Samples

Solution sample for the first experiment was taken from the drainage of an agricultural fertilizer manufacturer, one day before the experimental work. In the case of later experimental tasks, samples were created artificially. In order to maintain the same characteristics throughout all studies, synthesized samples have the same characteristics as real industrial wastewater samples. The wastewater samples were kept at 5 ^oC until the time of the experiment [38]. In order to imitate the identical NH_3^+, NO_3, and TN values in the first sample of industrial wastewater and its pH value, synthetic samples are created by adding the needed amount of ammonium hydroxide NH_4OH and ammonium nitrate NH_4NO_3 into distilled water. Analysis was conducted according to Standard Methods [39], [40]

2.3. Adsorbents (Borosilicate Glasses) Synthesis

Borosilicate glass samples (adsorbents: I, J, and K) were synthesized by the conventional melt quenching technique. The chemical composition of oxide glass consists of three components: former, modifier, and intermediate. In case of this study, the former of the glass composition is boron oxide B_2O_3 and silicon oxide SiO_2 together, so it is called borosilicate glass. Copper oxide (CuO) is the modifier of the glass composition, which was used to modify the properties of the glass compositions, such as reducing the melting point. The glass intermediate oxide (GIO) was used in the glass composition to create the bonds between the glass molecules and the modifier. To lower the melting point, sodium carbonate is utilized as a precursor to sodium oxide Na_2O. The chemical formula of used borosilicate glass samples (adsorbents: I, J, and K) is 25% B_2O_3–20% SiO_2 – 5% CuO – 5% GIO – 45%

Na_2O. GIO is Al_2O_3 for adsorbent (I), SnO for adsorbent (J), and Bi_2O_3 for adsorbent (K). Eq. (1) was used to determine the amount of each chemical constituent in the borosilicate glass composition based on its atomic weight. After calculating the weight of each chemical constituent for each borosilicate glass sample, all the constituents of one sample were combined and milled in a porcelain mill. The mixture was placed in the porcelain crucible for containment, and then it was heated to 1000 °C for 60 minutes for melting. When the melt reaches room temperature after melting process, it is shaped into a piece with its specific qualities. Then, the glass sample was ground into small particles of 125 - 63 µm by a grinding machine (Fritsch Mortar Automatic Grinder), that after a few hours have passed since the sample came out of the furnace, that to make sure the glass sample was completely formed and it acquired room temperature.

$$Q = A.W * P\% \quad \text{gm} \qquad \text{Eq.(1)}$$

Where: Q means the quantity of chemical constituent by grams, A.W is the atomic weight of chemical constituent, which was calculated by the atomic weight of its chemical elements, P is the percentage of the chemical constituent in the borosilicate glass composition. X Ray Diffraction analysis (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and Brunauer–Emmet–Teller (BET) analysis were carried out on adsorbents in powder case before adsorption process; Scanning Electron Microscope (SEM) was used before and after adsorption process.

2.4. Adsorption Process

The adsorbent dosage 1.5 g / 100 ml was added to the beaker, and then adding the solution sample to the adsorbent dosage. The mixture was stirred using a hot plate magnetic stirrer; the string rate was 300 rpm for 150 minutes at 40°C. Following the stirring stage, the liquid is filtered using a Buchner funnel with qualitative filter paper (its pore size of 0.45 µm). The spectrophotometer (HACH DR6000) is used for sample analysis. Adsorbent removal efficiency by percent (E) and the adsorption capacity (Q_t) were determined by Equation (2) and Equation (3), respectively:

$$E = 100\,(C_o - C_f) / C_o \qquad \text{Eq.(2)}$$

$$Q_t = ((C_o - C_t) / V) / m \qquad \text{Eq.(3)}$$

C_o means the initial concentration of contaminants (mg/L), C_t refers to the concentration of contaminants (mg/L) at time t, C_f is the final concentrations of contaminants (mg/L), V refers to the volume of solution sample (L), m is the adsorbent mass (g), and Qt shows the adsorption capacity of contaminant per gram of adsorbent (mg/g) at a time t.

3. RESULTS AND DISCUSSIONS

3.1. Characterizations of Adsorbents

3.1.1 XRD Analysis

X-Ray Diffraction analysis (XRD) was carried out to confirm the amorphous structure of adsorbents (I, J, and K). Bucker D8 Advance Diffractometer was employed in the two theta range between 10 and 80 degrees, in order to conduct the XRD analysis on adsorbents. The XRD patterns of adsorbents (I, J, and K) are shown in Figure (1). No crystalline peaks are seen in any of the XRD patterns, indicating that all adsorbents samples are amorphous.

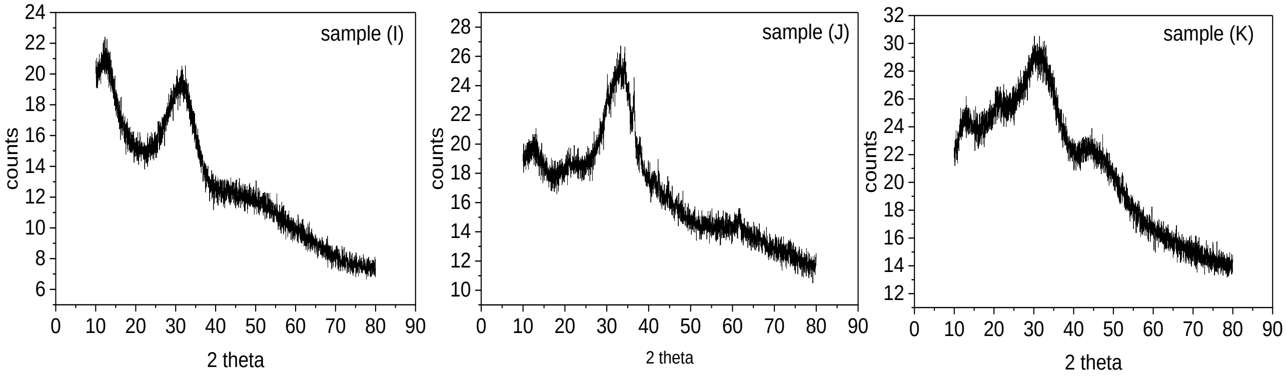

Figure 1. X-ray powder diffraction for adsorbents (I, J, and K).

3.1.2. FTIR Analysis

Fourier Transform Infrared Spectroscopy (FTIR) was performed to confirm the presence of all chemicals used in the borosilicate glass sample after synthesis process [41]. Platinum – ATR (Bruker Alpha) was employed in the wavenumber range of 450–4000 cm^{-1}. Figure (2a) shows the IR spectra for adsorbent K, the bending vibration peak of Si–O–Si appears in absorption peaks 473.5 cm^{-1}, and the stretching vibration peak of O–Si–O close to 800 cm^{-1}. The absorption peak close to 1187.26 cm^{-1} is the bending vibration peak of Si–O–Si, this synchronizes with the stretching vibration peak of BO_4 (antisymmetric). The bending vibration peak of BO_3 and anti-symmetric stretching vibration peak of BO_3 appears in absorption peaks close to 725.35 cm^{-1} and 1450.35 cm^{-1} are, respectively [42]. Theoretically, when a little amount of Al_2O_3 was added to borosilicate glass, Al^{3+} has priority to draw in free oxygen to form [AlO_4], gaining access to the SiO_2 structure to produce the more stable structure [42]. Furthermore, because of the lack of oxygen, basically exists as [BO_3] rather than [BO_4]. The borosilicate glass containing SnO or Bi_2O_3, achieved the same peaks as those previously described, as seen in Figures (2b and 2c), respectively, but with modest wavenumber changes due to the employment of a different glass intermediate oxide.

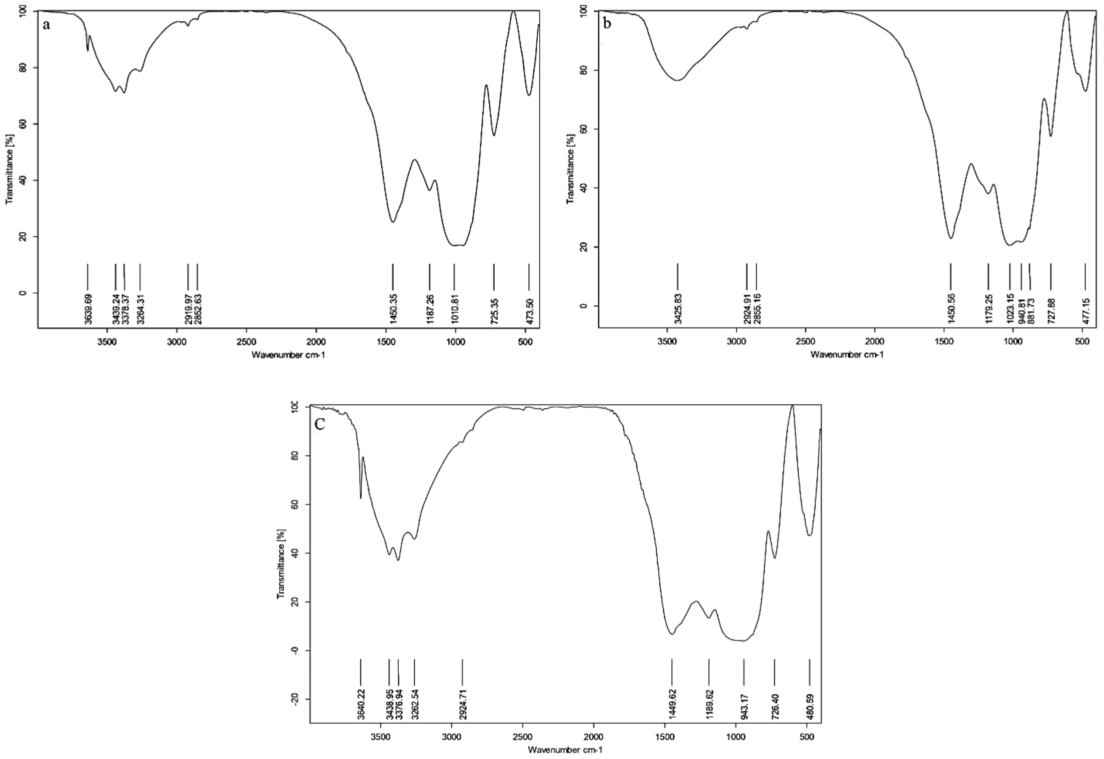

Figure 2. FTIR spectrum for borosilicate glasses, a): adsorbent I, b): adsorbent J, c): adsorbent K

3.1.2. BET Analysis

Brunauer–Emmet–Teller (BET) analysis was carried out to measure the surface area and average pore radius of adsorbents (I, J, and K) [43]. Nova touch LX^4 Quantachrome instrument version 1.21 was employed to determine the surface area and average pore radius of adsorbents, Table 1 displays the outcomes.

Table 1. The surface area and average pore radius of the adsorbents (BET analysis)

Oxide Glass	Surface Area	average pore radius
	m^2 / g	nm
I	29.84	1.80
J	45.69	1.56
K	18.57	1.60

Because they have an influence on the effectiveness of the adsorption process, the surface area and pore size of the adsorbents must be determined. The surface area reveals the presence of active spots that can take up molecules or atoms of contaminant. When the size of the adsorbent particles is reduced through the grinding process, the surface area rises for the same amount of adsorbent, which improves the efficiency of the adsorption process [44]–[46]. Also, both the arrangement of the adsorbent's pores and their size have a big effect on the efficiency of adsorbent. The size of adsorbent's pores controls the possibility of contaminant molecules entering them [47], where the adsorption process is achieved, but on the condition that the molecules of contaminant are smaller than the size of the adsorbent's pores. The arrangement of the pores, has a different impact if they appear in long isolated cylinders than if they are highly branched [48].

3.2. Intermediate Oxides

The intermediate oxide (network co-former) is used in the glass synthesis to re-establish the bonds between the glass molecules and the modifier, so as to retain the continuity of the structure. Where, the modifier is used to reduce the melting point, which in turn breaks the glass bonds. The three intermediate oxides used in the study were: aluminum oxide Al_2O_3, tin oxide SnO, and bismuth oxide Bi_2O_3, which were used in adsorbents I, J, and K, respectively. This is for monitoring the effect of intermediate oxides on the efficiency of borosilicate glass in removing contaminants (NH_3^+, NO_3, and TN). The effect of the intermediate oxides in the chemical composition on the removal efficiency of adsorbent is shown in Figure (3). The experimental work has been conducted under boundary conditions: adsorbent dosage 1.5 g/ 100ml, contact time 150 min, stirring rate 300 rpm, and temperature 40^{o}C. The pH value of the solution was 8.9, and the initial concentrations of NH_3^+, NO_3, and TN were 171 mg/L, 170.8 mg/L, and 363 mg/L, respectively. The ammonia (NH_3^+) removal efficiency with adsorbents I, J, and K is around 64%, 75%, and 77%, respectively. The nitrate (NO_3) removal efficiency with adsorbents I, J, and K is around 87%, 91%, and 90%, respectively. The total nitrogen (TN) removal efficiency with adsorbents I, J, and K is around 80%, 85%, and 86%, respectively. It's observed that the nitrate and total nitrogen removal efficiency of adsorbents J and K is approximately similar; ammonia (NH_3^+), nitrate (NO_3), and total nitrogen (TN) removal efficiency of adsorbent (I) is the least, as shown in Figure (3).

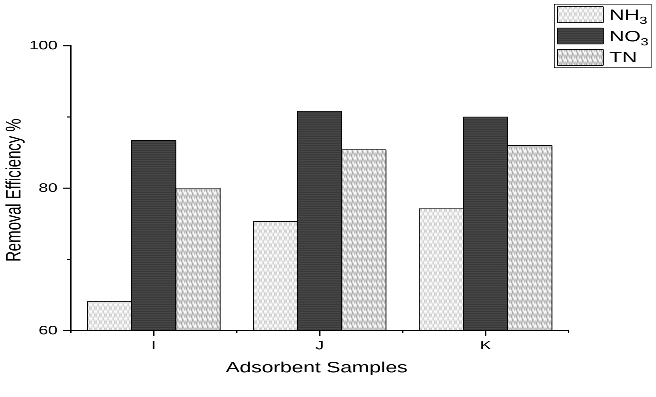

Figure 3. The Removal Efficiency of Adsorbents I, J, and K.

According to previous studies [24], it was discovered that improving adsorption efficiency does not require an increase in adsorbent surface area or pore size as long as the adsorbents have varied chemical compositions. By reviewing Table 1, this shows the specific surface area and the pore size of adsorbents. It was found that the largest surface area was to adsorbent (J), which was 45.69 m^2/g, and the largest pore radius was to adsorbent (I), which was 1.8 nm. Adsorbent (K) had the least value in surface area and the pore size. However, adsorbents J and K had almost the same adsorption performance, as shown in Figure (3), and they both achieved the best removal efficiencies of NH_3^+, NO_3, and TN. adsorbent (K) achieved the highest efficiency in removing ammonia and total nitrogen, which was very close to the efficiency of adsorbent (J). It was lower than adsorbent (J) in removing nitrate by a slight difference. This means that there are several factors that control the efficiency of the adsorption process. The surface charge of the adsorbent and the contaminants has a major influence, such as the importance of the effect of surface area and pore size. However, when utilizing the same adsorbent, the specific surface area plays a significant effect. As noted in previous studies, which showed that reducing adsorbent particle size leads to an increase in adsorbent surface area, and this encourages the presence of active sites and so boosts the process's effectiveness [49]–[51]. In this work, comparisons are made between three adsorbents with various properties and chemical compositions. It turned out that although one adsorbent's surface area may be greater than another's, the surface charge of the adsorbent and contaminants is crucial for attracting contaminants and enhancing adsorption capacity [52], [53], as the surface charge is affected by the pH value of solution [54], [55]. Additionally, it is challenging to complete the adsorption process for this adsorbent because the molar volume of the contaminant may be greater than the pore radius of the adsorbent, as the pores size and its arrangement has a major effect on possibility of contaminants' molecules entering the adsorbent's interior [43], [47], [48]. All of this indicates that the surface area and pore size are not a sufficient indicator about the efficiency of one adsorbent over another, and the difference in the type of the intermediate oxide has an effective role in changing the efficiency of the adsorbent in the adsorption process. Where tin oxide SnO and bismuth oxide Bi_2O_3 gave adsorbents (J and K, respectively), these had higher adsorption efficiency than the adsorbent (I) synthesized using aluminum oxide Al_2O_3.

3.3. Characteristics of Solution Sample

The amount of contaminants in industrial wastewater fluctuates over time, depending on; the amount of product produced, how water is used for manufacturing processes, the workers' personal use, and cleaning purposes. This also affects the wastewater's pH level. This study looked at the effect of both contaminants concentration and pH level on the effectiveness of the adsorption process, using the three types of borosilicate glass (adsorbents: I, J, and K).

3.3.1 Contaminant Concentration

The effect of the initial contaminants concentrations was investigated in six cases (1, 2, 3, 4, 5, and 6). Table 2 shows the concentrations of NH_3^+, NO_3, and TN in each case. The experimental work has been conducted under boundary conditions: adsorbent dosage 1.5 g/ 100ml, contact time 150 min, stirring rate 300 rpm, and temperature 40°C. The pH value of the solution was 8.9. The results of experimental work show in Figure (4).

Table 2. The concentrations of NH_3^+, NO_3, and TN in each case

Case	NH_3^+	NO_3	TN
1	28 mg/L	28 mg/L	60 mg/L
2	57 mg/L	55 mg/L	125 mg/L
3	85 mg/L	85 mg/L	190 mg/L
4	113 mg/L	110 mg/L	250 mg/L
5	140 mg/L	136 mg/L	316 mg/L
6	170 mg/L	168 mg/L	380 mg/L

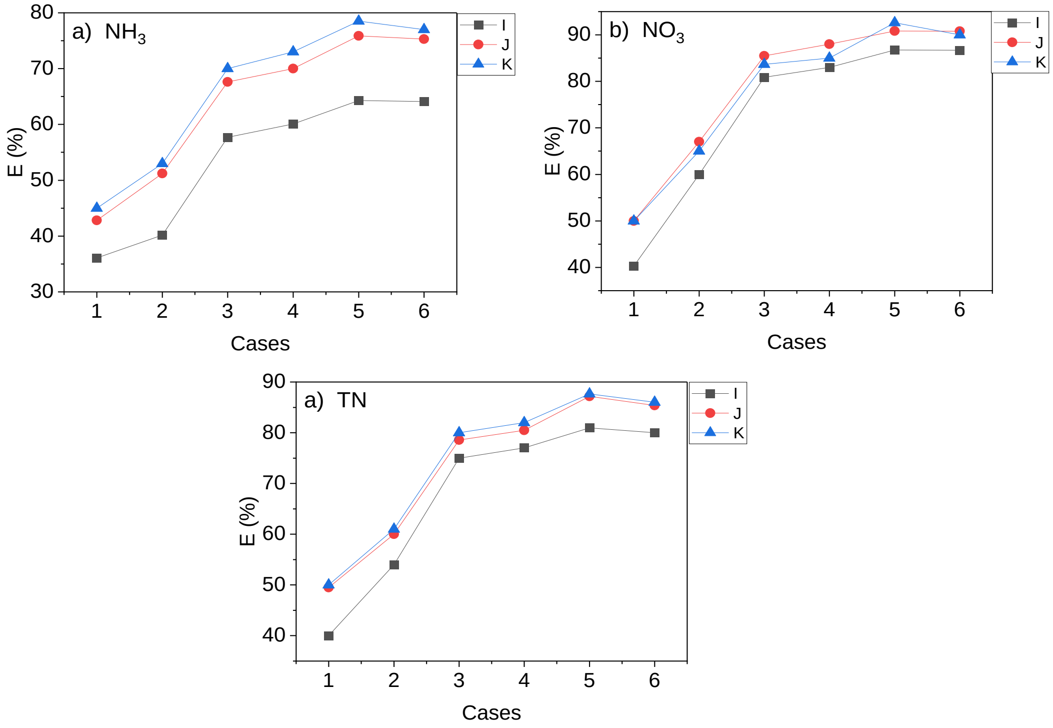

Figure 4. The effect of initial contaminants concentration on adsorption efficiency (a): NH_3^+, (b): NO_3, and (c): TN

As Figure (4) shows, at case 1, the removal efficiencies of NH_3^+, NO_3, and TN were around 36%, 40%, and 40%, respectively, then the removal efficiencies of NH_3^+, NO_3, and TN increased to around 64%, 87%, and 81%, respectively at case 5, that with adsorbent (I). At case 1, the adsorbent (J) had NH_3^+, NO_3, and TN removal efficiencies 43%, 50%, and 50%, respectively, then they increased to around 76%, 91%, and 87%, respectively at case 5. At case 1, the adsorbent (K) had NH_3^+, NO_3, and TN removal efficiencies around 45%, 50%, and 55%, respectively, then NH_3^+, NO_3, and TN removal efficiencies reached to around 79%, 93%, and 88%, respectively at case 5. In case of low contaminants concentrations, the ions might be attracted to active sites of adsorbent, at the increasing ion concentrations, more ions have the capability to occupy active sites. That refers to the differences in the mechanism of ion adsorption, ion adsorption is subjected to adsorbent pores, paths of the arranged lattice, and the need for interchangeable cations' displacement [56]–[58]. The results confirm that excessive initial contaminants concentration leads to increase in the adsorbent capacity to adsorb but to a certain limit. If it is considered that surface adsorption is the ion removal driving force that means increasing the initial concentration of contaminant ions leads to driving force improvement [59], [60]. After case 5, the removal efficiency decreased by a very small value that is almost unnoticeable. At case 6, NH_3^+, NO_3, and TN removal efficiencies were 64.1%, 86.7%, and 80%, respectively for adsorbent (I), 75.3%, 90.8%, and 85.4%, respectively for adsorbent (J), and 77%, 90%, and 86%, respectively for adsorbent (K). It is concluded, the removal efficiency after the concentration case 5 began to decrease with increasing of contaminants concentration, that refers to the adsorbent active sites are no longer sufficient to accommodate higher molecular numbers of contaminants. Thus, the adsorption efficiency of the adsorbent decreased because of active sites are saturated with contaminant ions [7], [61]–[63].

3.3.2 pH Value of Solution

pH value of the solution sample has an important effect on the contaminants' adsorption processes, as it affects the contaminants' ionization and the adsorbent surface charge. The effect of pH on the removal efficiency of adsorbents (I, J, and K) was studied from 4.1 to 11 with a contact time of 150 minutes, initial glass dosage of 1.5 g/100 ml, stirring rate 300 rpm, temperature 40°C, and initial concentration of NH_3^+ =168 – 171 mg/L, NO_3 =155 – 171 mg/L, and TN=360 – 380 mg/L. pH value was controlled after preparing solution samples by adding 0.1M NaOH or 0.1M HCl solution. The results of experimental work are illustrated in Figure (5). The best ammonia (NH_3^+)

removal efficiency achieved at pH value of 8.9, as it observed in Figure (5a). Using the adsorbents I, J, and K, the effectiveness of NH_3^+ removal at pH value 4.1 was 55.7%, 66.5%, and 68.2%, respectively. It increased to 64.1%, 75.3%, and 77.1%, respectively at pH value 8.9. Then, it decreased to 55.5%, 68.1%, and 70.1%, respectively at pH value 11. Ammonia exists in the water solution in two forms; un-ionized (NH_3) and ionized (NH_4^+) [64], [65]. Ammonium ions must compete with hydrogen ions for exchange sites under acidic conditions, where the ionized form is predominate. Additionally, a number of contaminants that fill adsorbent pores may be eliminated by hydrogen ions at lower pH levels [66]. While progressively converting from ammonium ions to aqueous ammonia in alkaline conditions [67], [68]. Therefore, the best removal efficiencies which were achieved at pH value of 8.9. The results agree with the study was conducted by ligand exchange onto a Cu(II)-loaded chelating resin [69]. The results pointed that, ~~the~~ pH has a significant effect on ammonia removal by adsorbents I, J, and K since it can affect both the character of the contaminant ions and the character of the adsorbent itself [70], [71].

Figure (5b) shows the effect of pH on nitrate removal efficiency. The best results was achieved at pH 4.1, the effectiveness of NO_3 removal was 90.1%, 95.2%, and 93.8%, that with the adsorbents I, J, and K, respectively. It decreased to 86.7%, 90.8%, and 90%, respectively at pH value 8.9, and then continued to decrease until it reached to 55.5%, 68.1%, and 70.1%, respectively at pH value 11. The reason for improving the removal of nitrate at the acidic condition is that the negative charge on the surface decreases due to the increasing of protons in solutions. Thus, ~~the~~ pH of the system decreases and the number of positively charged sites increase. At pH lower than 7, the oxides in solution tends to form an aqua complex to yield a positively charged surface [72], a positively charged surface site on the adsorbent prefers the adsorption of the nitrate anions due to electrostatic attraction [73]. It was not possible to study the effect of the pH value on TN removal efficiency, as the initial concentration of TN changes with the change in the pH value of solution sample.

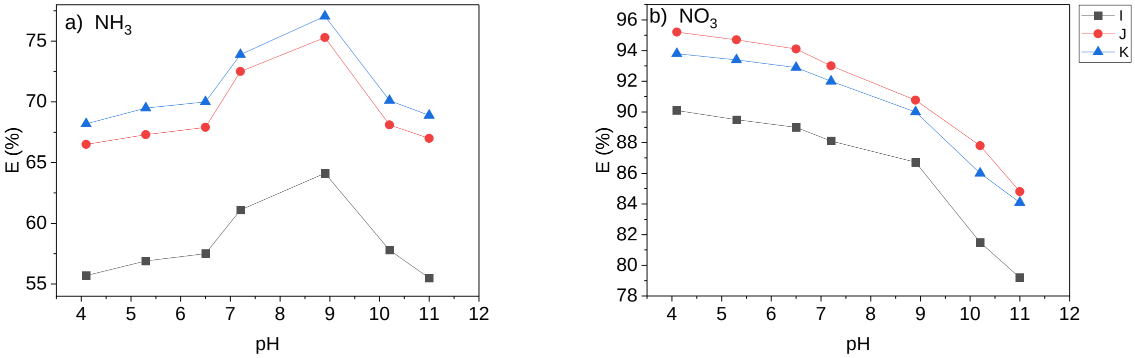

Figure 5. The effect of pH value on adsorbents removal efficiency (a): NH_3^+, and (b): NO_3

3.4. Scanning Electron Microscope (SEM) for Adsorbents

Scanning Electron Microscope (SEM) was used to observe the morphology of adsorbents (I, J, and K) before and after adsorption process. Quanta FEG 250 Scanning Electronic Microscope was employed to achieve this purpose. Figure (6) shows the pores on the surface of adsorbents (I, J, and K) before the adsorption process. Figure (7) shows the blockage of these pores with granules of the contaminant's atomics after the adsorption process, as tiny chunks of adsorbate atomics appear in glass samples surfaces.

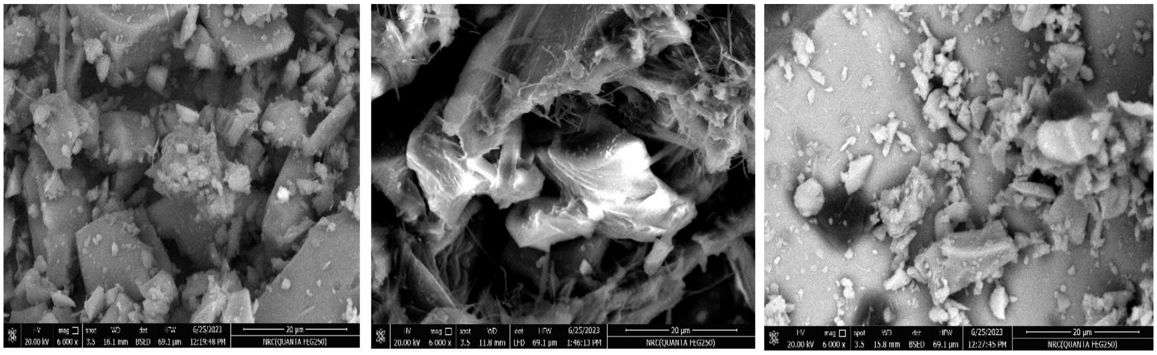
(I) before adsorption process (J) before adsorption process (K) before adsorption process

Figure 6. SEM figures of adsorbents (I, J, and K) before adsorption process.

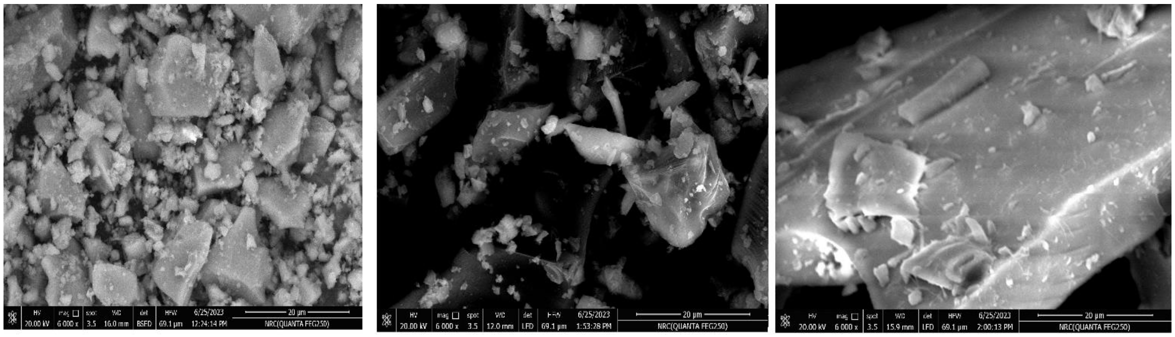
(I) after adsorption process (J) after adsorption process (K) after adsorption process

Figure 7. SEM figures of adsorbents (I, J, and K) after adsorption process.

3.5. Adsorption Isotherms

Langmuir and Freundlich isotherm models are crucial for validating the findings of adsorption-related experimental studies, and describe the equilibrium relation between adsorbent and contaminants. The Langmuir theory is predicated on the assumptions that the equilibrium desorption and adsorption rates are the same, that the surface of the adsorbent material is homogeneous, and that the interaction between the adsorbate molecules and the adsorbent surface is not significant. The linear form of the Langmuir Equation (4) was employed [74].

$$C_t/Q_t=(1/Keq)+(C_t/Q_{max}) \qquad \text{Eq. (4)}$$

The parameter K_{eq} refers to Langmuir constant; Q_{max} means the maximum adsorption capacity (mg/g); C_t is the contaminants concentration at time t (mg/L); Q_t means the adsorption capacity at time t (mg/g).

C_t/Q_t vs C_t can be plotted to obtain the linear outline (Fig.8). The linear equation's slope and intercept can be used to obtain the Langmuir constants Q_{max} and K_{eq}, respectively.

The non-homogeneous nature of the adsorbent surface is supported by Freundlich theory Equation (5). The underlying premise of the theory is that the adsorption sites on an adsorbent surface have various adsorption energies.

$$\log Q_t= \log K_f + (1/n) \log C_t \qquad \text{Eq. (5)}$$

The parameters K_f and n refer to Freundlich constants, these constants can be determined from the slope and the intercept from linear outline of log Q_t vs log C_t (Fig.9), respectively.

Fitting the experimental data to these isotherm models and taking into account the higher values of correlation coefficients for the respective lines' slopes and intercepts, those shown in Table (3), that shows various isotherm constants and their correlation coefficients were determined for the adsorption of NH_3^+, NO_3, and TN onto adsorbents (I, J, and K) at boundary conditions and characteristics of solution sample [adsorbent dosage = 1.5 g/100mL, contact time = 30, 60, 90, 120, and150 min, Temp=40^{0}C, pH = 8.9, and contaminants concentrations: NH_3^+ =168 – 171 mg/L, NO_3 =155 – 171 mg/L, and TN=360 – 380 mg/L]. The results indicate that the contaminants (NH_3^+, NO_3, and TN) investigated on adsorbents (I, J, and K) are in agreement with the Langmuir and Freundlich isotherm models, as the regression coefficient (R^2) is in range (0.999-0.996) for the Langmuir and Freundlich isotherm models.

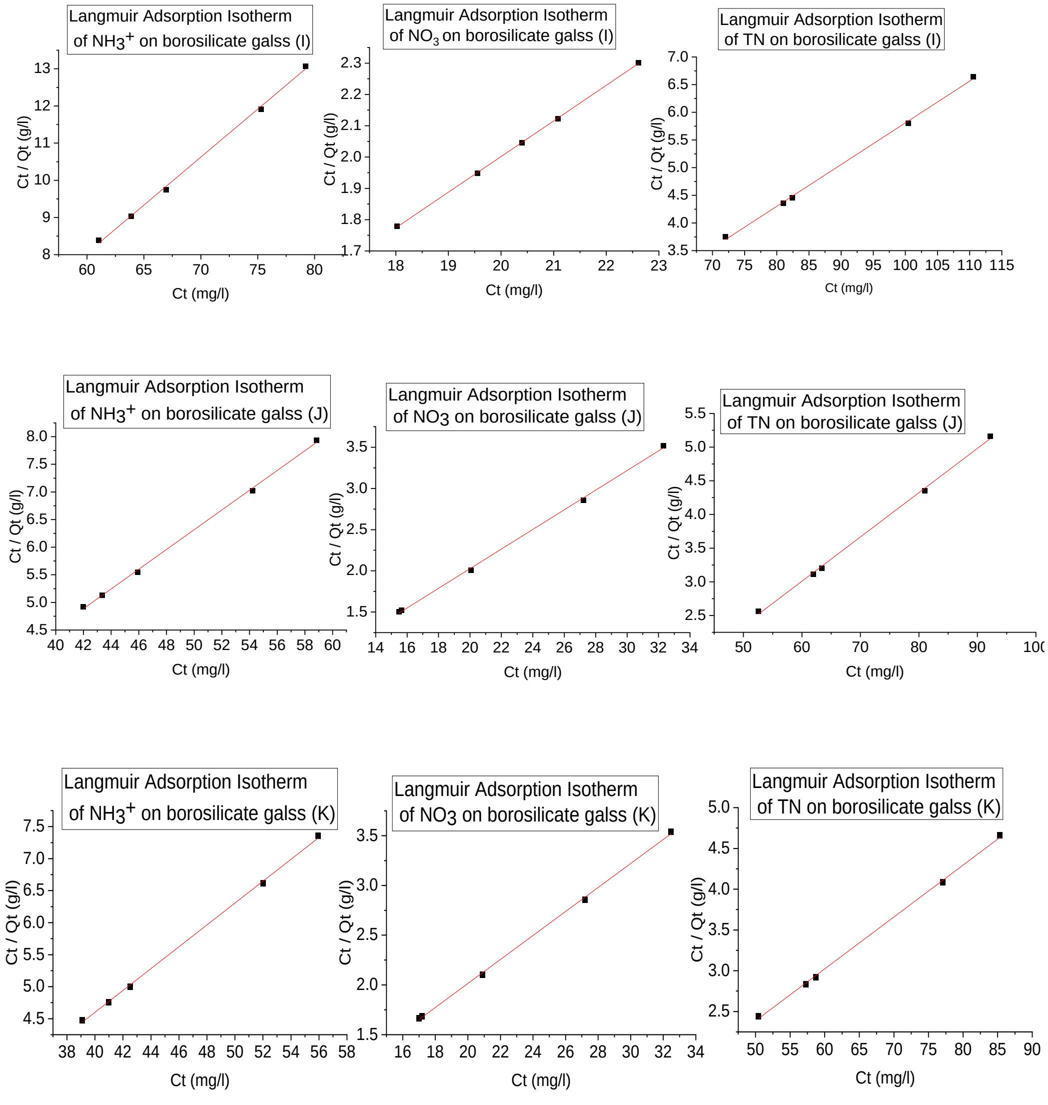

Figure 8. Langmuir adsorption Isotherm for NH_3^+, NO_3, and TN onto adsorbents (I, J, and K)

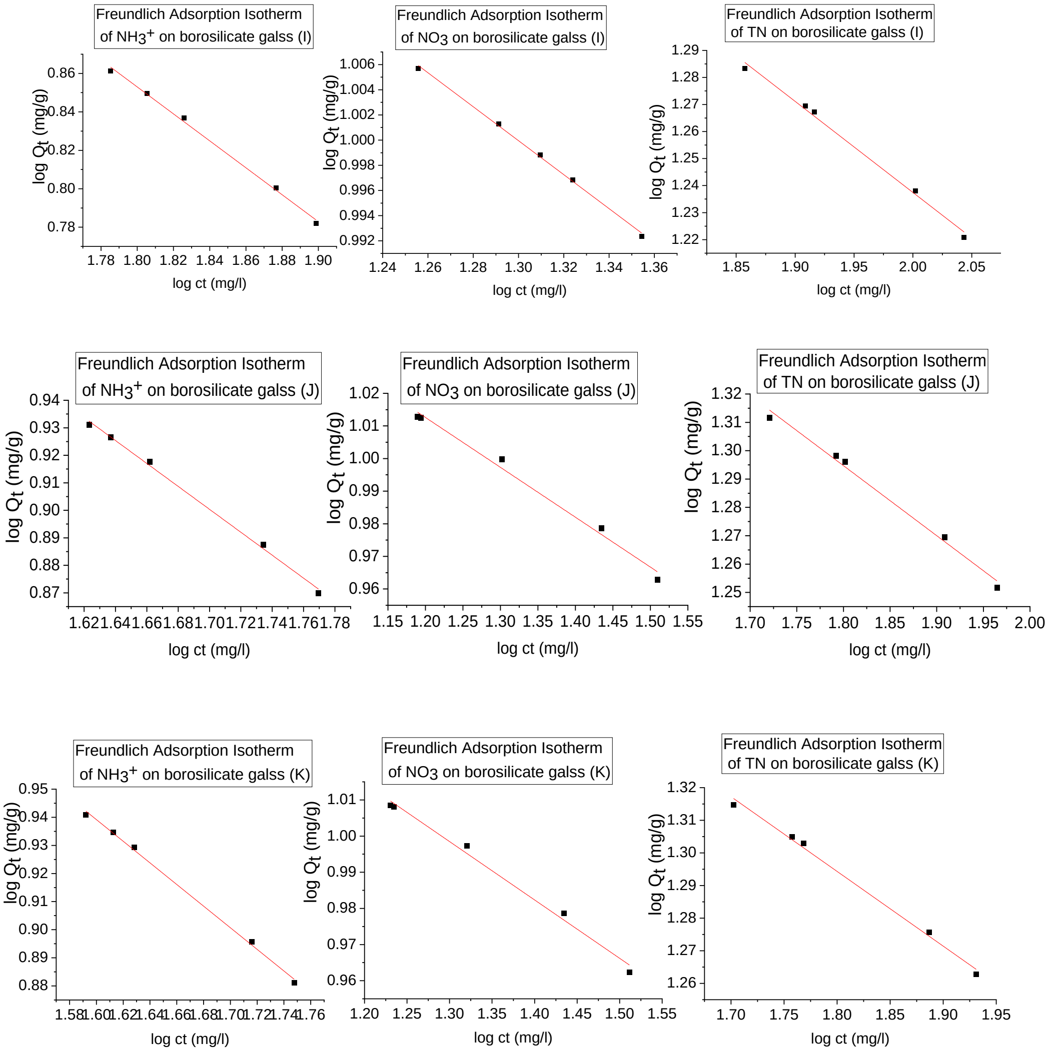

Figure 9. FREUNDLICH ADSORPTION ISOTHERM FOR NH3+, NO3, AND TN ONTO ADSORBENTS (I, J, AND K)

Table 3. Various Isotherm Constants and Their Correlation Coefficients

Adsorbent	Contaminants	Langmuir model, Eq. (4)			Freundlich model, Eq. (5)		
		K_{eq} (L/mg)	Q_{max} (mg/g)	R^2	Log K_F (mg/g)	1/n	R^2
I	NH_3^+	0.065	3.81	0.997	0.69	0.6965	0.998
	NO_3	0.056	3.52	0.999	0.88	0.67	0.999
	TN	0.202	14.52	0.998	0.17	1.23	0.997
J	NH_3^+	0.122	5.4	0.998	3.06	1.04	0.998
	NO_3	0.146	5.9	0.997	2.9	0.95	0.998
	TN	0.47	20.39	0.998	2.596	0.526	0.996
K	NH_3^+	0.158	6.12	0.998	2.82	0.917	0.998
	NO_3	0.12	5.34	0.998	3.08	1.05	0.998
	TN	0.52	21.1	0.999	2.5	0.5	0.997

CONCLUSIONS

According to the study's findings, borosilicate glasses have noticeable efficient as adsorbents in removal of NH_3^+, NO_3, and TN From industrial wastewater. Adsorbents (I, J, and K) were characterized using several techniques such as XRD, FTIR, and BET. Three intermediate oxides in chemical composition of borosilicate glass were used, namely aluminum oxide Al_2O_3, tin oxide SnO, and bismuth oxide Bi_2O_3, that to synthesize three different samples of borosilicate glass (adsorbents : I, J, and K). Adsorbents J and K achieved the best performance in removing NH_3^+, NO_3, and TN, which were synthesized using intermediate oxide SnO and Bi_2O_3, respectively. Adsorbents I, J, and K increased the removal efficiency of NH_3^+, NO_3, and TN with increasing the initial concentration of contaminants, but only up to a certain limit of initial concentration of contaminants, where after this limit the removal efficiency began to be not noticeable decrease. The best efficiency of ammonia removal achieved with pH value 8.9, but the highest efficiency of nitrate removal was in acidic case (pH value 4.1). The surface shape of adsorbents (I, J, and K) before and after the adsorption process was clarified using SEM, which showed the blockage of pores on the surface of the samples by grains of atomic contaminants after the adsorption process. The adsorption process of contaminants (NH_3^+, NO_3, and TN) onto the three samples of adsorbents (I, J, and K) are in agreement with the Langmuir and Freundlich isotherm models.

CONFLICT OF INTEREST

The authors declare that there is not any conflict of interest regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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