



Research article

The removal of nickel and lead ions from aqueous solutions using green synthesized silica microparticles

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ARTICLE INFO

Keywords:

Materials science
Materials chemistry
Nanotechnology
Silica microparticles
Adsorption
Heavy metal ion
Lead ion
Nickel ion

ABSTRACT

Silica microparticles were synthesized from sugarcane bagasse via a green synthetic technique. The prepared silica microparticles were used to remove lead and nickel ions from their separate solutions. Microscopic analysis shows that the synthesized silica particles are spherical with good monodispersed properties. The average particle diameter of the silica microparticles is estimated to be about 432 nm. Batch adsorption experiment was employed to examine the influence of adsorbent dosage, contact time, heavy metal ion concentration and pH on the adsorption efficiency of the synthesized silica microparticles in removing the studied lead (Pb²⁺) and nickel (Ni²⁺) ions from their respective solutions. An increase in adsorbent dosage, heavy metal ion concentration, contact time and pH led to an increase in the percentage removal of Pb²⁺ and Ni²⁺ metal ions from their individual solutions. The adsorption process of Pb²⁺ ion onto the synthesized silica microparticles followed the Langmuir adsorption isotherm ($R^2 = 0.961$), while, the nickel ion (Ni²⁺) followed the Freundlich isotherm ($R^2 = 0.869$). The adsorption process of the studied heavy metals (Pb²⁺ and Ni²⁺) in their separate solutions favours pseudo-second-order reaction model (R^2 , 0.978 and 0.999) over the pseudo-first-order reaction model.

1. Introduction

Heavy metals can be described as naturally existing elements whose atomic weight and density is at the minimum 5 times larger than that of water [1]. Industrial discharge contain organic and inorganic pollutants, including heavy metals [2]. These metals are carcinogenic and/or toxic and as such dangerous to living things [1, 2]. Heavy metals of utmost concern from several industrial wastes include nickel (Ni), mercury (Hg), lead (Pb), copper (Cu), chromium (Cr), cadmium (Cd), arsenic (As) and zinc (Zn) [1]. These heavy metals can be found in pesticides, fertilizers, metal complex dyes, bleaching agents, fixing agents (they are introduced to dyes to improve the adsorption of dye onto the fibres) and pigments [3]. Nickel is carcinogenic and can also lead to pulmonary fibrosis, lung and kidney problems, skin dermatitis and gastrointestinal distress [4]. Similarly, lead is dangerous to the health of humans and can damage the liver, brain functions, reproductive system and kidney [5]. The removal of heavy metals from wastewaters have been achieved by several techniques such as reverse osmosis, reduction, chemical oxidation, ultra-filtration, chemical precipitation, adsorption, ion exchange, and

electrodialysis [6]. Among the aforementioned methods, the adsorption technique has been established to be among the most reliable because the other methods possess some inherent limitations which include low efficiency, low sensitivity in operating conditions, large quantity of sludge generation and costly disposal. The adsorption technique is seen as a more favourable alternative for the expulsion of heavy metals as it yields treated effluents with high-quality, flexibility in design, the adsorbent can be regenerated [6].

Adsorption of heavy metals has been carried out by a previous study using metallic oxides particles [7]. For this study, we focused on silica which is classified as a metalloid. Metalloids are elements that exhibit the external characteristics of a metal but behaves chemically more as a non-metal in their oxides [8]. In the form of oxides, silica can be manipulated into particles with nano or micrometer range to exhibit unusual properties due to their small sizes and high density of edge surface sites. Silica, among other oxides, has been applied in the field of photo-catalysis, catalysts and magneto-electronics, solar-cells and gas-sensors [9]. Myriads of techniques such as sol-gel method [10], Stöber technique [11] and micro-emulsion modified technique [12] have

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been used to synthesize nano or micro sized silica particles. However, these techniques have numerous drawbacks such as, difficulty in tuning their morphology, phase composition, particle sizes as well as supplementary step of purification. This study, therefore, made use of extraction and precipitation techniques to solve these problems [13]. The advantages of these techniques over the aforementioned techniques are the absence of processes with high amount of energy, such as reduction in chemical amounts due to calcination, less toxic chemical consumption. The extraction stage involving the pretreatment process of the silica particles helps to remove the metallic impurities present in the particles, leading to the preparation of nano or micro silica particles with high purity.

Sugarcane bagasse which is a fibrous residue has been established to be a natural source of silica microparticles [12, 14]. Orthosilicic acid, a major component of soil which is usually deposited in the stem and leaves of sugar cane is the origin of silica particles in sugarcane bagasse [15, 16].

This study, therefore, synthesizes silica microparticles from sugarcane bagasse which is considered to be an agricultural waste. The prepared silica microparticles were used to remove nickel and lead ions from the individual solutions of Pb and Ni ions. The fact that the studied silica microparticles were synthesized using agricultural wastes (sugarcane bagasse) of no economic value and simple cheap chemicals (HCL and NaOH) to synthesize the adsorbent (silica microparticles), makes this method economical and as well, aids the cleanup of sugar cane waste which would have caused environmental pollution.

2. Experimental

2.1. Materials

Concentrated hydrochloric acid, sodium hydroxide pellet, potassium iodate, lead (II) nitrate, nickel (II) nitrate, starch and sodium thiosulphate were purchased from Sigma Aldrich and used without further purification. Distilled water was used throughout the reaction. Sugarcane bagasse samples used in this study was collected from sugarcane juice sellers in Benin City, Edo State, Nigeria.

2.2. Silica microparticles extracted from sugarcane bagasse ash

The Silica microparticles used in this study were synthesized as described by a published procedure with slight modification [17]. The sugarcane bagasse (SCB) was washed thoroughly with distilled water to remove dirt and soil and then oven-dried at 90 °C. 1N HCl was added to the sample to remove metallic impurities present. The mixture was soaked in water bath with temperature of 75 °C. The sample was filtered, washed for several times to remove metallic ions in the sample and dried again in an oven with temperature of 90 °C. The SCB was introduced into a muffle furnace at a temperature of 700 °C and left for 4 h for the production of sugarcane bagasse ash (SCBA). The SCBA was placed inside a two-neck flask containing 1M sodium hydroxide (NaOH) solution. To obtain a sodium silicate solution, it was heated in a water bath for 1 h with a temperature of 90 °C. Precipitation of the sodium silicate was performed by adding 1 mol/L hydrochloric acid (HCl) solution until the pH of 7 is attained. The mixture was kept for at least 18 h at room temperature for the precipitated silica to completely solidify. The slurry was thereafter filtered and rinsed with distilled water repeatedly until a neutral pH was achieved. The formed solid was dried at 80 °C to get the silica microparticles using a laboratory oven.

2.3. Characterization of micro-silica (NS)

The functional groups and morphology of the synthesized silica microparticles were investigated using Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM) respectively.

2.4. Removal of heavy metal from separate solutions of Pb²⁺ and Ni²⁺ ions

A known quantity of lead and nickel nitrate salts (Pb²⁺ and Ni²⁺ ions) were dissolved in two separate beakers (Figure 1) containing de-ionized water to prepare stock solutions of 1000 mg/L. Adsorption studies were carried out by homogenizing a constant amount of 0.5 g silica microparticles with 10 ml of 0.1 M solution of lead (II) nitrate and nickel (II) nitrate respectively at room temperature for 10 min. The adsorption experiments in this study were carried out at a controlled pH of 6. To examine the effect of an elevation in the amount of adsorbent on the adsorption of metal ions, different adsorbent doses varying by 0.5 g increments between 0.5 to 2.5 g were added into five different beakers with 20 ml of solutions each containing 50 mg/L of lead or nickel ions. To study the adsorption efficiency of the synthesized adsorbent (silica microparticles) on the concentrations of lead and nickel ions in their respective solutions, the concentration of the metal ions were varied in duplicate as follows: 10.0, 20.0, 30.0, 40.0–50.0 mg/L at room temperature. To investigate the time required for the heavy metal adsorption to attain equilibrium, samples were allowed to stand at different time intervals (10, 20, 30, 40 and 50 min). Based on the contact time, it was found that 40 min was sufficient to attain the equilibrium for the lead and nickel ions adsorption. For studies based on pH, 1 mol/L concentration of hydrochloric acid (HCL) and sodium hydroxide (NaOH) solutions were used to control the solution pH in a range of 1–8, while keeping other adsorption conditions constant. It was found that a pH value of 6 was optimum for adsorption experiments to be conducted.

Atomic absorption spectrophotometer was thereafter, used to analyze the concentration of lead and nickel ions in the residues. For computing Langmuir and Freundlich parameters, which define the performance of the adsorbent, pH was maintained at 6, contact time at 40 min, concentration of nickel and lead ions at 50 mg/L and amount of adsorbent at 2.5 g. The adsorption data was fitted into Langmuir and Freundlich adsorption isotherms to establish the isotherm that best describes the adsorption process of the studied heavy metals onto the prepared silica particles. For result accuracy, adsorption studies were carried out in triplicate at a room temperature of 23 °C and standard deviation (SD) was computed.

2.5. Statistical analysis

The significant differences in the obtained data were investigated using analysis of variance (ANOVA). SPSS (Statistical Package for Social Scientist) was employed to compare the mean of the estimated data.

3. Results and discussion

3.1. Functional groups of the as-synthesized silica microparticles

The functional groups of the synthesized silica microparticles are revealed in Figure 2. They were examined by FTIR in wave number range of 4500–500 cm⁻¹. The emergence of the symmetric vibration of Si–O and asymmetric vibration of Si–OH are attributed to the absorbance peak at 944 cm⁻¹. The pronounced peak at 1091 cm⁻¹ is due to the anti-symmetric motion of silicon atoms in siloxane bonds. The peaks at 3485 cm⁻¹ and 3226 cm⁻¹ may be due to the presence of water moisture which may have been absorbed from the environment.

3.2. Morphology of the prepared silica particles

Figure 3 shows the scanning electron micrograph of the prepared silica particles. The SEM analysis showed good level of monodispersed spherical microparticles. The average particle diameter of the as-synthesized silica particles is placed at about 432 nm (the measurement was obtained using image J application). The obtained spherical shape is similar to the observation of Mohd et al. [18]. However, the

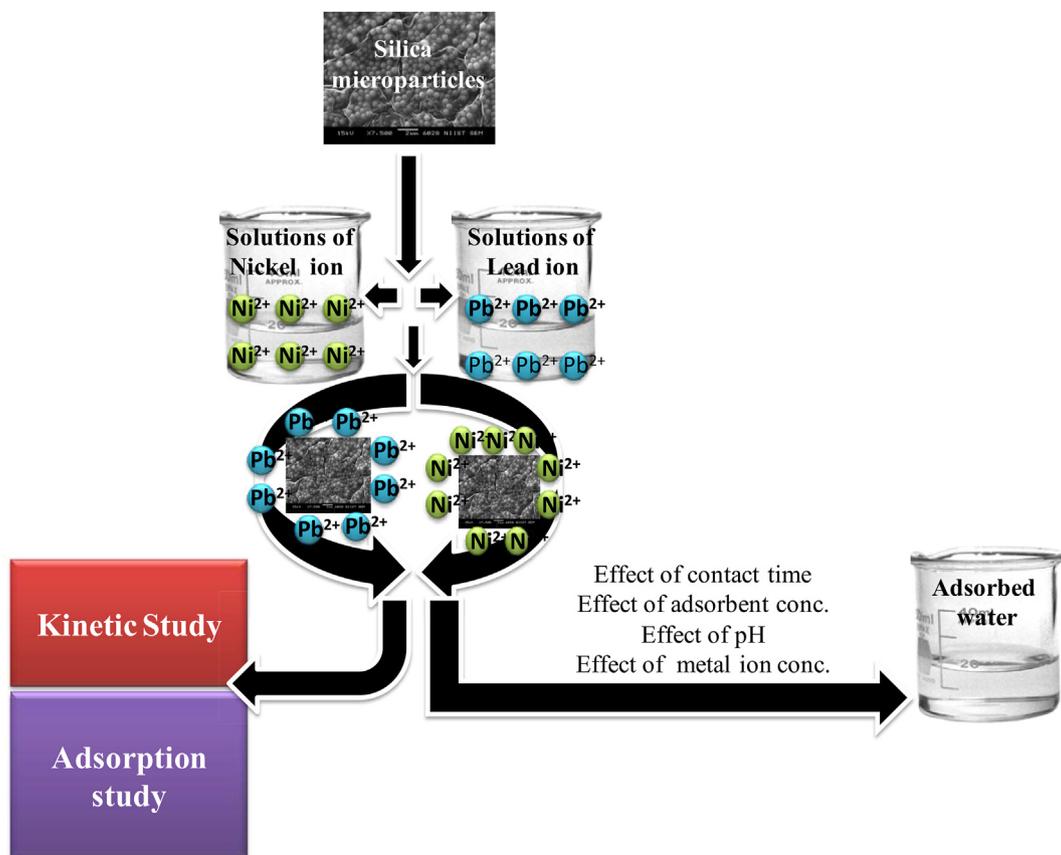


Figure 1. Flow chart indicating a summary of the whole study.

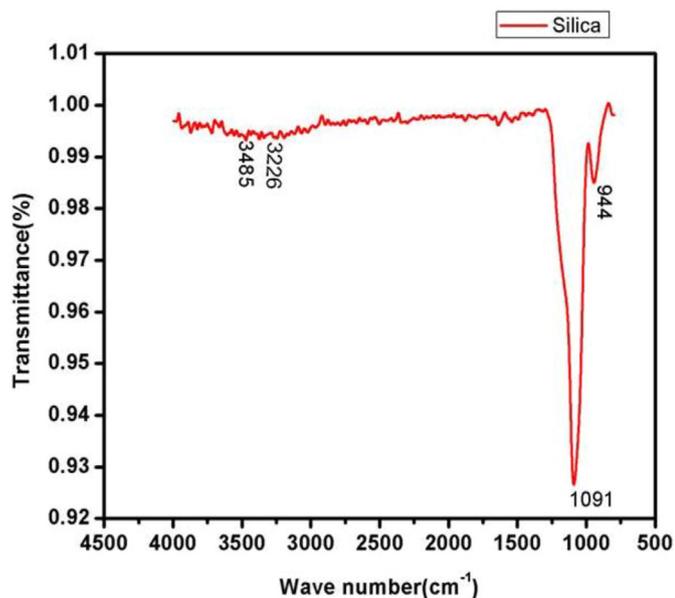


Figure 2. FTIR spectra of as-synthesized silica microparticles.

morphology of the synthesized silica microparticles that was obtained in this study, is less agglomerated and more monodispersed with a better periodic arrangement of particles.

3.3. Effect of contact time

The adsorption of heavy metals from the separate solutions of Pb and Ni ions using the synthesized silica microparticles as an adsorbent with

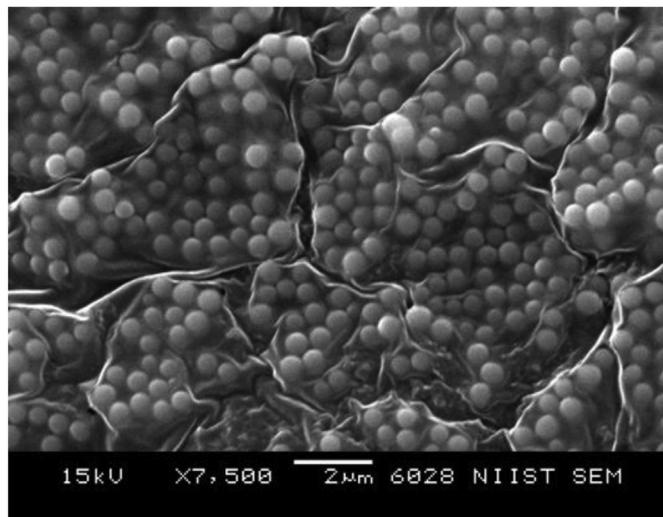
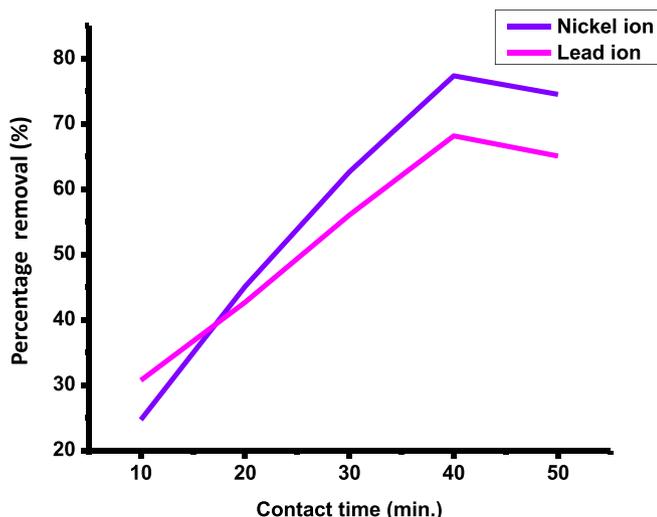


Figure 3. Scanning electron micrograph of silica microparticles.

respect to contact time was examined. The study was carried out under a pH of 6, a room temperature (23 °C) and ion concentration of 50 mg/l. The percentage of metal ions (Pb²⁺ and Ni²⁺) adsorbed at variable contact times of 10, 20, 30 and 50 min from the individual solutions of Pb²⁺ and Ni²⁺ ions is depicted in Table 1 and Figure 4. Experimental results revealed that the adsorption efficiency (%) of the studied adsorbent (silica microparticles) on the metal ions under study varied significantly with contact time at P < 0.05 (Table 1) as there was a rapid adsorption of the heavy metal ions onto the prepared silica particles as the adsorbent increased. The percentages of nickel and lead ions

Table 1. Effect of contact time on adsorption of heavy metals.

Contact time (min)	Nickel ion (Ni ²⁺)	Lead ion (Pb ²⁺)
	Percentage removal (%)	Percentage removal (%)
10	24.70 ± 0.20 ^a	29.72 ± 0.02 ^a
20	45.10 ± 0.10 ^b	42.7 ± 0.30 ^b
30	62.66 ± 0.22 ^c	56.06 ± 1.17 ^c
40	77.36 ± 0.03 ^c	68.17 ± 0.02 ^c
50	74.52 ± 0.12 ^d	65.06 ± 0.02 ^d

**Figure 4.** Effect of contact time on adsorption of Pb²⁺ and Ni²⁺ ions.

adsorbed were observed to increase from an initial percentage adsorption (%) of 24.70 ± 0.20 and 29.72 ± 0.02 to an optimum adsorption (%) of 77.36 ± 0.03 and 68.17 ± 0.02 for the studied nickel and lead ions respectively as the contact time increases from 10 min to 40 min. This therefore means that the equilibrium time was attained at a contact time of 40 min. The time at which the aforementioned optimum adsorptions were reached is known as the equilibrium time. At this stage, the amount of heavy metals adsorbed is not affected by any further increase in adsorption time. The short optimum time observed for the heavy metal ions may be due to the small particle diameter (432 nm) of the as-synthesized silica particles. This promotes a faster mobility rate of the lead and nickel ions from the individual bulk solutions of lead and nickel ions onto the energetic sites of the silica surface. It may also be due to the overlapping of adsorption site caused by overcrowding of the adsorbent particles [19]. Beyond this contact time (40 min), a decrease in adsorption (%) from 77.36 ± 0.03 to 74.52 ± 0.12 for lead ion and 68.17 ± 0.02 to 65.06 ± 0.02 for nickel ion was observed. Benhamou et al. [20] obtained a similar result with the adsorption of Cd²⁺, Co²⁺, Cu²⁺ and Pb²⁺ metal ions using ordered mesoporous silica as the adsorbent. This result has economic and practical consequences because the studied low cost silica adsorbent could be utilized in the removal of nickel and lead ions from industrial scale waste-water within a short period of time.

Means with different alphabet remarks in the same column are significantly different at 5 % probability level ($P < 0.05$). The superscripts a, b, c represents the statistical significance of the experimental data.

3.4. Effect of adsorbent dosage

To determine the effect of varying the adsorbent dosages on the percentage of heavy metal ions adsorbed (Pb²⁺ and Ni²⁺), the as-synthesized adsorbent (silica microparticles) was varied from 0.5 g to

2.5 g. This experiment took place under a temperature of 23 °C, at a contact time of 10 min under conditions of constant pH 6. Table 2 and Figure 5 reveals the effect of varying the dosages of adsorbent on the removal of the studied metal ions with an initial concentration of 50 mg/L for Ni²⁺ and Pb²⁺. At $P < 0.05$, the adsorption efficiency (%) of the studied silica microparticles (adsorbent) on the heavy metals under examination were observed to change significantly with adsorbent dosage (Table 2). Experimental data revealed that the percentage adsorbed (%) increased from 20.28 ± 0.01 to 60.48 ± 0.12 for Nickel (II) ion and 33.58 ± 0.03 to 76.04 ± 0.04 for lead (II) ion as the dosage of silica particles increased from 0.5 g to 2.5 g (Table 2, Figure 5). The increase in adsorption as the adsorbent dosage increases may be due to the ratio of insufficient number of the adsorbing species to a larger number of readily available sites on the surface of the adsorbent at higher dosages. This finding indicates that adsorption is virtually directly proportional to the amount of the dosage. Previous studies have observed a large number of available sites that are exchangeable at higher adsorbent dosages during the uptake of heavy metal ions [21]. In a nutshell, this study can be described as economical and of practical implications because a small quantity of silica microparticles (0.5 g–2.5 g) has recorded a reasonable adsorption percentage of nickel and lead ions from their individual solutions.

Means with different alphabet remarks in the same column are significantly different at 5 % probability level ($P < 0.05$). The superscripts a, b, c represents the statistical significance.

3.5. Effect of heavy metal ion concentration

To examine the effect of metal concentration on the adsorbed metal ions, variable concentrations of heavy metals (Ni²⁺ and Pb²⁺) were dispersed in distilled water. The concentration of nickel ion (Ni²⁺) and lead (Pb²⁺) added to the distilled water were varied between 10 mg/L to 50 mg/L respectively. This study was carried out under the conditions of room temperature (23 °C), contact time (10 min) and constant pH 6. The influence of an increase in metal concentrations on the adsorption of metal ions is depicted in Table 3 and Figure 6. The adsorption efficiency (%) of the investigated adsorbent on the analyzed heavy metals were seen to improve significantly with heavy metal ion concentration at $P < 0.05$ (Table 3). A similar result was observed by a previous study [22]. As the concentration of metal ions increases from 10 mg/L to 50 mg/L, the percentage adsorption (%) increased from 15.06 ± 0.05 to 44.92 ± 0.11 for nickel ion and 17.20 ± 0.02 to 47.20 ± 0.10 for the lead ion. The observed increase in the heavy metals (Ni²⁺ and Pb²⁺) removed may be due to the more improved specific area of adsorbent and the increase in the likelihood of collision between the adsorbent particles and metal ions [23]. However, there was a rapid decrease in the nickel ion concentration that was adsorbed from 47.50 ± 0.10 to 37.50 ± 0.10 . The exact point in the curve where the decrease was noticed is known as the equilibrium point. At this point, any additional increase in the lead ion concentration has no effect in the heavy metal adsorption as seen in Figure 5.

3.6. Effect of solution pH

The electrostatic interactions' existing between the heavy metal ions in the aqueous solution and the surface of the synthesized silica microparticles is a major factor that could influence the adsorption of heavy metals from the separate solutions of Pb and Ni ions. This nature of interactions is majorly regulated by the solution pH. In a typical experiment, the pH of several samples was controlled from 1–8 at an optimum time and adsorption amount to determine the optimum pH of adsorption. The effect of varying the pH on the sorption of the studied lead and nickel ions was examined while keeping other reaction parameters constant. Table 4 and Figure 7 revealed the influence of pH on the amount of heavy metal adsorbed from the individual solutions of Pb and Ni ions with different level of intensity. The analyzed adsorbent capacity towards the removal of the investigated heavy metals from the separate solutions of

Table 2. Effect of adsorbent dosage on adsorption of heavy metals.

Dosage (g)	Nickel ion (Ni ²⁺)	Lead ion (Pb ²⁺)
	Percentage removal (%)	Percentage removal (%)
0.5	20.28 ± 0.01 ^a	33.58 ± 0.03 ^a
1.0	35.16 ± 0.02 ^b	40.48 ± 0.12 ^b
1.5	45.58 ± 0.04 ^c	50.22 ± 0.10 ^c
2.0	55.58 ± 0.01 ^d	63.62 ± 0.02 ^d
2.5	60.48 ± 0.12 ^e	76.04 ± 0.04 ^e

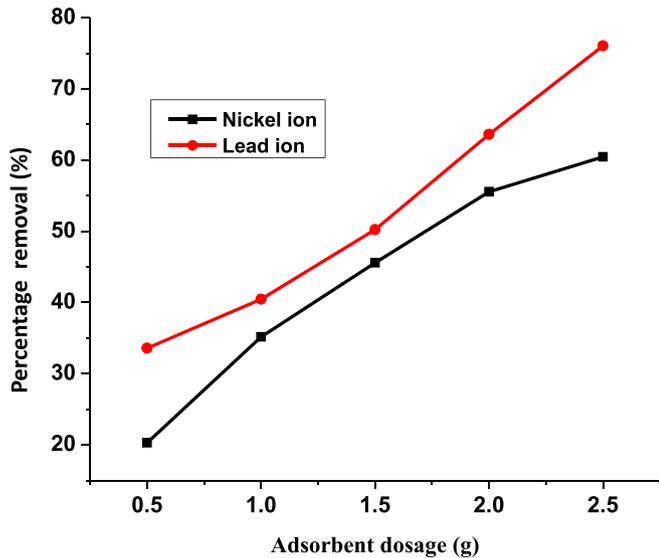


Figure 5. Effect of adsorbent dosage on adsorption efficiency of silica particles from separate solutions of Pb and Ni ions.

Table 3. Effect of Heavy metal ion concentration on adsorption of heavy metals.

Conc. Of heavy metals in water (mg/L)	Nickel ion (Ni ²⁺)	Lead ion (Pb ²⁺)
	Percentage removal (%)	Percentage removal (%)
10.00	15.06 ± 0.05 ^a	17.20 ± 0.02 ^b
20.00	26.42 ± 0.02 ^b	14.70 ± 0.00 ^a
30.00	35.70 ± 0.00 ^c	20.80 ± 0.10 ^c
40.00	44.92 ± 0.11 ^c	47.50 ± 0.10 ^c
50.00	38.48 ± 0.04 ^d	37.50 ± 0.10 ^d

Means with different alphabet remarks in the same column are significantly different at 5 % probability level (P < 0.05).

Pb and Ni ions can be said to have been enhanced significantly with increase in the pH (P < 0.05, Table 4). It is evident from the result that the adsorption of the lead and nickel ions by the silica microparticles (adsorbent) was highly dependent on the pH as both spectra were observed to increase with an increase in pH. This result is consistent with the observation of Zhu et al. [24].

For pH region <6, the sorption capacity of heavy metal ions was observed to increase as the pH increases. However, at pH > 6, a decrease in the percentage of lead and nickel ion removed (%) by the adsorbent (silica microparticles) was observed. The reduction in adsorption may be due to the precipitation of metal hydroxides on the surface of the silica microparticles adsorbent which may have resulted from the hydrolysis of the metal ions. Maximum uptake of 71 ± 0.20 % and 68 ± 0.30 % for nickel and lead ions apiece was attained at an optimum pH of 6 (Figure 7). This is an indication that the deprotonation of sorbent surface would be more favourable for the individual solutions of Pb and Ni ions

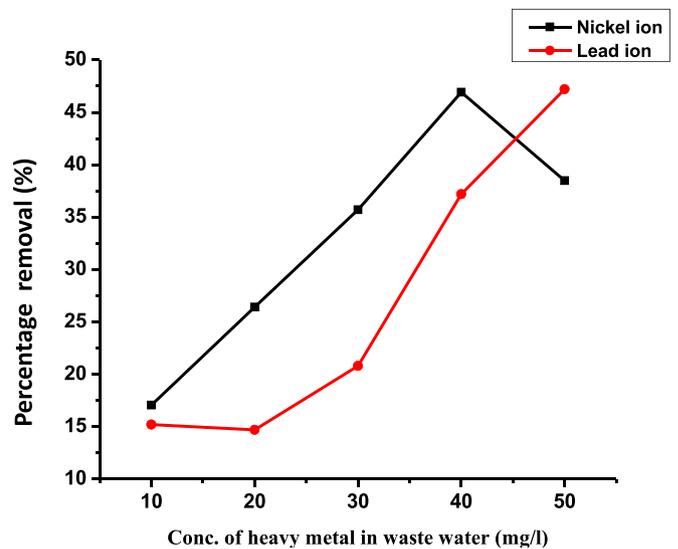


Figure 6. Effect of concentration of Ni²⁺ and Pb²⁺ ion on the percentage removal (%) of silica particles.

whose pH does not exceed 6 [25]. The observed increment in deprotonation may have led to increased sites with negative charges, thereby, enhancing the forces of attraction between the metal ions and the sorbent surface. Contrarily, the removal of the metal ions from the separate solutions of Pb²⁺ and Ni²⁺ ions at lower pH levels was greatly hindered probably because of the competition between the hydrogen ion (H⁺) and metal ions for the same adsorption sites and protonation of the adsorbent surface. It has been established that heavy metal ions have tendencies to form metal hydroxides at pH level greater than 6 [26]. In summary, this study agrees with the already existing fact that, when trying to obtain an efficient metal adsorption, one of the major factors that should be put into consideration is the pH [27, 28, 29, 30]. Based on the result from this study, it is recommended that the adsorption of heavy metals from wastewaters using silica microparticles should be carried out with an optimum pH of 6. It is therefore recommended that this finding be incorporated in the removal of heavy metals from waste or used waters before disposer.

3.7. Kinetic study

Adsorption kinetics is significant for the understanding of adsorption processes. Adsorption kinetics can be examined by investigating the correlations between adsorbed metal ion and the time required for the adsorption to take place. The mechanisms involving the kinetics that control the adsorption process were studied by analyzing the adsorptive uptake of metal ions (Pb²⁺ and Ni²⁺ ion) from their solutions onto the as-

Table 4. Effect of pH on adsorption of heavy metals.

pH	Nickel ion (Ni ²⁺)	Lead ion (Pb ²⁺)
	Percentage removal (%)	Percentage removal (%)
1	42 ± 2.00 ^a	40 ± 0.20 ^a
2	47 ± 0.50 ^b	46 ± 0.50 ^b
3	54 ± 1.00 ^c	51 ± 1.00 ^c
4	61 ± 0.20 ^d	57 ± 0.30 ^d
5	66 ± 0.10 ^e	63 ± 0.30 ^f
6	71 ± 0.20 ^f	68 ± 0.30 ^g
7	65 ± 1.00 ^e	62 ± 0.40 ^e
8	62 ± 0.20 ^d	57 ± 0.50 ^d

Means with different alphabet remarks in the same column are significantly different at 5 % probability level (P < 0.05).

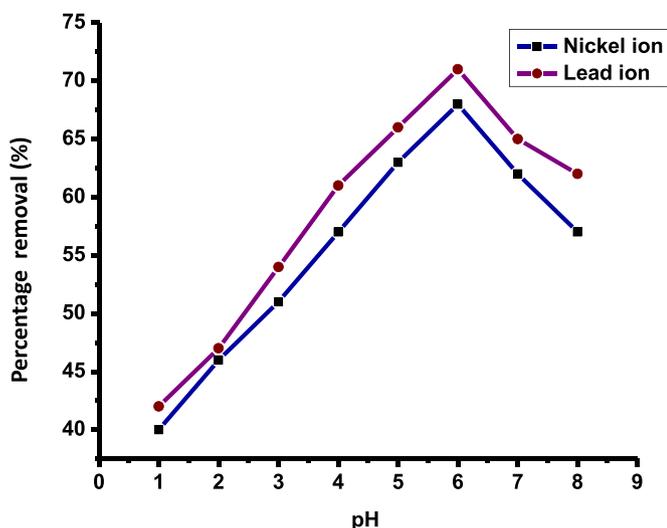


Figure 7. Effect of adsorption efficiency on pH.

synthesized silica microparticles (adsorbent) at different time intervals. The obtained experimental data were fitted into the pseudo-first-order [31] (Equation 1) and pseudo-second-order models (Equation 2); [31].

$$\log(q_e - q_t) \log q_e - \frac{k}{2.303t} \tag{1}$$

$$\frac{1}{q_t} = \frac{1}{k_{2q_e}} + \frac{t}{q_e} \tag{2}$$

Where q_e and q_t are the sorption capacities at equilibrium (mmol/g) at any time t (min.), K is the equilibrium rate constants for first-order and second-order adsorption. The obtained experimental data for lead and nickel ions were fitted into the pseudo-first-order and pseudo-second-order reaction models (Figure 8(a, c & b, d)). The result showed that

the process employed by the adsorbent (silica microparticles) in removing the lead and nickel ions from the individual solutions of Pb and Ni ions fitted best to the pseudo-second-order reaction model (Figure 8 (b & d)) when compared to the pseudo first order reaction model (Figure 8(a & c)) because its fitting degree (R^2) was observed to be closer to unity than the pseudo first order reaction model (Figure 8(b & d)). The correlation coefficients for the linear plots of t/q_t against time for the adsorption of the studied metal ions (lead and nickel ion) were observed to be 0.978 and 0.999 respectively for the pseudo-second-order rate law.

Whenever an adsorbent comes in contact with a solution, the process of adsorption of heavy metal ions (Pb^{2+} & Ni^{2+}) usually occur via three pathways [32]: 1) the adsorbate moved from the bulk solution to the external boundary film layer of liquid surrounding the surface of an adsorbent particle; 2) the attachment of the adsorbate onto the surface of the adsorbent is usually rapid and accompanied by an energy that corresponds to the nature of the binding process (chemical adsorption, physical adsorption or the combination of both adsorption process); and 3) adsorbate dispersed further into the internal adsorption sites of the adsorbent.

The fact that the adsorption of the studied metal ions (Pb^{2+} and Ni^{2+} ion) in the separate solutions of Pb and Ni ions fitted best to the pseudo-second-order model is an indication that the rate-limiting step of the adsorption process may be a chemical sorption process involving valency forces via sharing of electrons between sorbate and sorbent. Also, two nature of adsorption kinetics can be stipulated for this type of model [33]: sluggish adsorption at the initial stage which indicates a step by step adsorption of the studied metals at the surface of the silica microparticles [33] and initial swift adsorption which was probably caused by electrostatic attraction.

3.8. Adsorption isotherm

Adsorption isotherms can be employed to predict the fitting parameters and behaviour of sorbent towards various sorption systems [34]. The two most commonly used isotherms are the Langmuir and Freundlich adsorption isotherm models. Freundlich adsorption isotherm was

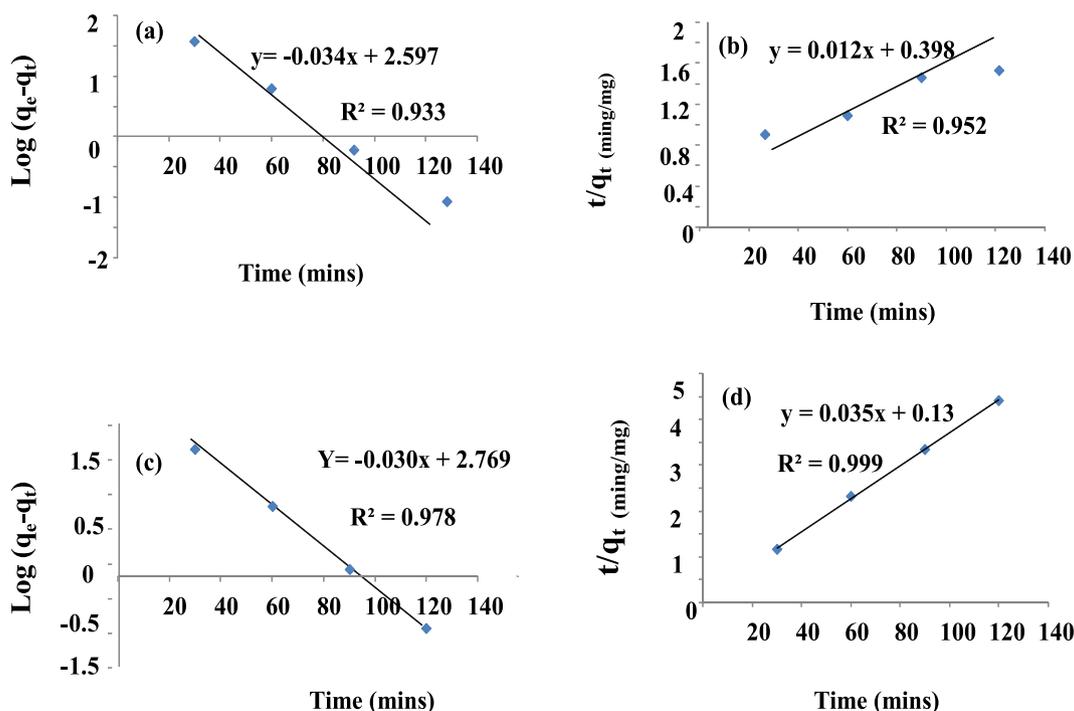


Figure 8. Adsorption of heavy metals on silica microparticles for pseudo-first-order/pseudo-second-order model for (a & b) Lead ion (Pb^{2+}) (c & d) Nickel ion (Ni^{2+}).

developed for heterogeneous system, and it proffers the theory of multilayer adsorption on the sorbent surface. The Langmuir adsorption isotherm is based on the theory that the adsorption of metal ions takes place on homogeneous adsorbent surfaces. This consequently results in the adsorbed metal ions having a monolayer arrangement. Also, the energy produced from the adsorption system is deemed constant [34]. The absence of movement of the material adsorbed and the mono-layer adsorption are major factors on which this isotherm is built on. To examine the best suited model for the adsorption of nickel and lead ions; data were inserted into the Langmuir and Freundlich adsorption isotherm models [35, 36]. The mechanism of metal ion adsorption from an aqueous solution by the adsorbents was investigated using Langmuir adsorption isotherm in accordance with Eq. (3) [35].

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m} \tag{3}$$

Where C_e is the adsorbate concentration at equilibrium, q_m is the capacity of maximum adsorption, q_e is the capacity of adsorption observed at equilibrium, K_L is the equilibrium constant of adsorption, q_m is the maximum adsorption capacity of the adsorbent. Figure 7 revealed a linear correlation between C_e and C_e/q_e for the metal ions adsorbed onto the silica particles (adsorbent). The correlation coefficient (R^2) which was estimated to be 0.961 is very good. The fact that the R^2 value of 0.961 obtained for lead ion is very close to unity after fitting its data into the Langmuir isotherm graph (Figure 9a) when compared to the R^2 value of 0.471 obtained from its Freundlich adsorption isotherm graph

(Figure 7c) is a strong indication that the adsorption process of lead ion onto the surface of the prepared silica particles (adsorbent) correlated more with the Langmuir adsorption isotherm. The linear plot revealed by the lead ion adsorption in Figure 9a is also additional evidence that shows that its adsorption onto the silica particles obeys the Langmuir model. This means that the maximum coverage of the lead ion onto the surface of the silica particles took place on a monomolecular layer on the adsorbent surface.

For the nickel ion, the results of the data that were fitted into the Langmuir and Freundlich isotherm adsorption model showed that the Freundlich isotherm best described the adsorption of the nickel ions. The R^2 value from the Freundlich isotherm was estimated to be 0.869. This value is very close to unity when compared to the correlation coefficient (0.250) obtained from the Langmuir adsorption curve. And also, n was observed to be less than 1 ($n < 1$). Freundlich equation is used to interpret adsorption data over a specific concentration range. This equation is normally used to describe surfaces that are highly heterogeneous [37, 38]. Freundlich adsorption isotherm is represented by Eq. (4):

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \tag{4}$$

Where, $1/n$ and K_f are constants of Freundlich isotherm which signify the adsorption capability and intensity of adsorption, respectively. Base on the linear form of Freundlich equation, the graph of $\log q_e$ against $\log C_e$ (Figure 9 (b & d)), were used to extrapolate Freundlich equilibrium constants. The degree of nonlinearity between adsorption and

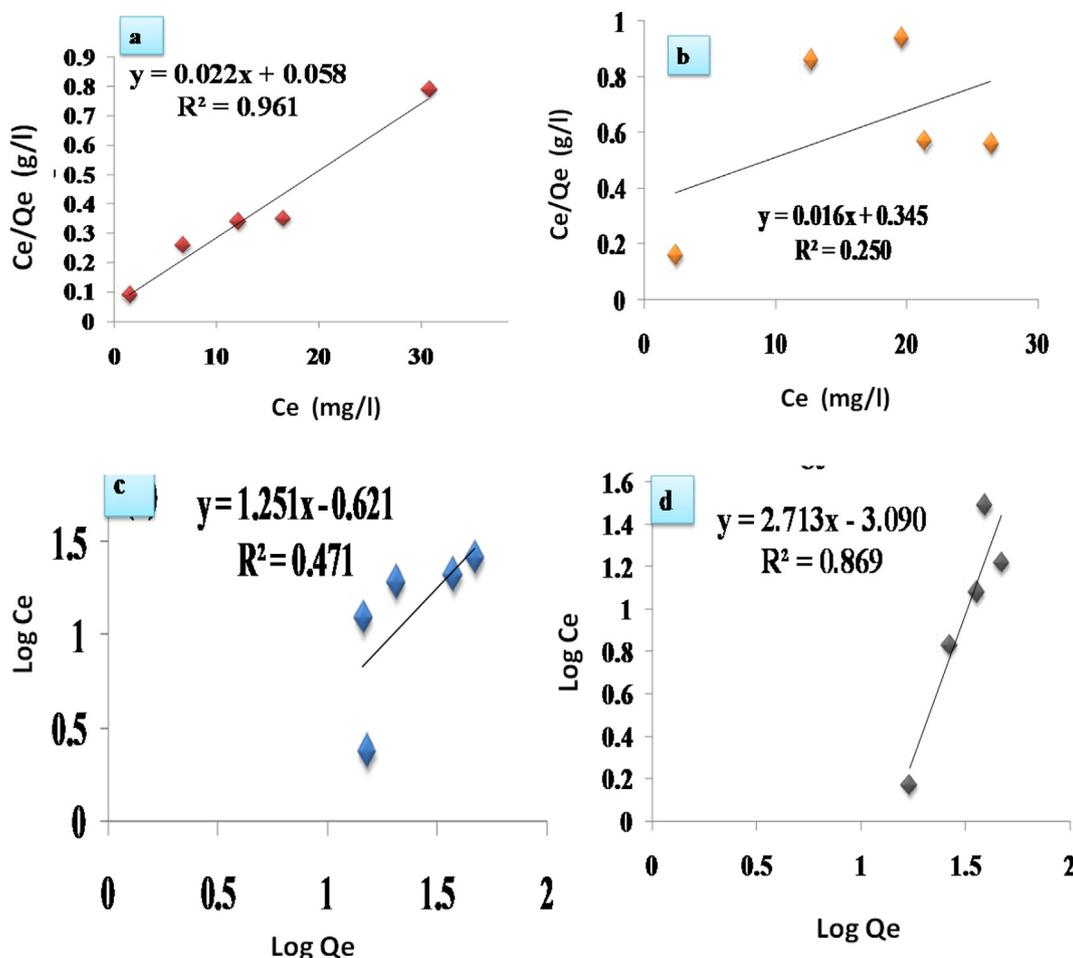


Figure 9. (a) Langmuir isotherm on the adsorption of lead ion (b) Langmuir isotherm on the adsorption of nickel ion (c) Freundlich isotherm on the adsorption of lead ion (d) Freundlich isotherm on the adsorption of nickel ion.

concentrations of solution is represented by n . Adsorption becomes a physical process, chemical process and linear when $n > 1$, $n < 1$ and $n = 1$ respectively.

4. Conclusion

Spherical shaped silica microparticles were synthesized from sugarcane bagasse via a green synthetic approach. The as-synthesized silica particles were used to remove lead and nickel ions from aqueous solutions which were contaminated with these heavy metal ions using adsorption technique. A study on the effect of metal ion concentration, contact time, adsorbent dosage and pH on the adsorption of Pb^{2+} and Ni^{2+} ions from their separate solutions revealed that an increase in metal ion adsorption up to a certain level as the aforementioned parameters increased. The adsorption of the lead ion takes place on a monomolecular layer on the adsorbent surface, making the adsorption process a surface phenomenon while that of the nickel ion was observed to be a chemical process as the nickel ion chemically interacted with the silica particles. Also, the adsorption process of metal ions (Pb^{2+} and Ni^{2+}) from their separate solutions fitted best to the pseudo-second-order reaction model.

Declarations

Author contribution statement

Ikhazuagbe Hilary Ifijen: Analyzed and interpreted the data; Wrote the paper.

Anastasia B. Itua: Performed the experiments.

Muniratu Maliki, Christie O. Ize-Iyamu, Stanley O. Omorogbe: Analyzed and interpreted the data.

Aireguamen I. Aigbodion: Contributed reagents, materials, analysis tools or data.

Esther U. Ikhuoria: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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