Fabrication of Nano-composite silica fume using Green microwave solvent-less technique for Pb(II) extraction

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Abstract
In the present work, Pb(II) is extracted from aqueous solutions using a Nano-composite of silica fume (SF@NPs) modified with quinoline derivative: 3-aminoquinoline (SF-3AQ@NPs) through the Green microwave synthesis. The conditions of the microwave technique (power and time) were studied. The optimum power and time adequate for the microwave synthesis of SF-3AQ@NPs were 20W for 5 min. SF@NPs and its modified phases were characterized by FT-IR, TEM, X-ray, and SEM analysis before and after modification. The nanoscale of SF@NPs and SF-3AQ@NPs was determined using TEM analysis. Parameters of extraction study in the batch method were also evaluated. The maximum adsorption capacity of Pb(II) on SF@NPs and SF-3AQ@NPs were 0.114 and 0.679, respectively. Also, the maximum removal efficiency (= 89.25%) with SF-3AQ@NPs than SF@NPs led to choosing it for removal of Pb(II) from different real water samples.

1. Introduction

The green microwave solvent-less technique has a new approach to the synthesis of solid support. This can be attributed to the immense potential and the well-known benefits of this technique, such as it has a rather quick reaction time when compared to regular procedures using conventional heating techniques. Furthermore, the adsorbent was effectively modified via green microwave synthesis, and its reactions can be carried out on solid supports without the need for solvents [1]. So, the green microwave solvent-less technique was used for the synthesis of many adsorbents [1-5].

On the other hand, due to its many advantages over other methods, including its higher preconcentration factor, lower waste generation, lower matrix effect, use of less toxic solvents, ability to regenerate a solid phase easily, and thus greater reusability, the solid phase extraction (SPE) method has emerged as a potent tool for the enrichment/separation of metal ions. For the preconcentration, separation, and determination of toxic metal ions like Pb(II), Cu(II), Fe(III), and others, it can be employed more effectively than other techniques [6–9]. The use of waste materials as solid phase extractors for the removal of toxic metal ions from aqueous solutions has received a lot of attention due to its economic benefits and high removal efficiency, which is attributed to many functional groups [2, 10, 11]. From these waste materials, Silica fume (SF) was selected as an appropriate solid phase extractor because it is non-toxic, inexpensive, has traditionally been regarded as a waste product, and has a particularly large surface area [11]. Additionally, these smooth-surfaced sub-micron particles are

very negatively charged, which is advantageous for bonding with positively charged metal ions. Furthermore, it has been demonstrated that the surface of SF significantly binds metal ions via surface complexation [12, 13]. Furthermore, the presence of SF in nanoscale forms (SF@NPs) gives it significant advantages in extraction processes with large surface areas. To create a novel SF@NPs-based material that is capable of chelating heavy metal ions such as Pb(II) in this situation, SF@NPs could be treated with organic functional groups that are quinoline derivatives. Quinoline derivatives have the potential to be used as organic modifiers on material surfaces to extract and remove some toxic metal ions such as Pb(II). They form stable complexes with Pb(II) due to their structure and the positioning of the functional groups along the surface, also their complexes which are formed with metal ions are only weakly soluble in water [14].

Due to its ease of extraction and processing, lead has been utilized as a metal for thousands of years. However, due to its environmental aggregation and high mobility, lead is a poisonous metal and is widely regarded as an element of high toxicity [15, 16]. Because lead is a hazardous metal, it can seriously harm people's health. Nearly all of the body's organs and systems are susceptible to its effects, but lead toxicity's principal victims are the neurological system, particularly in young children, and blood and brain diseases [17]. For the general public, water is one of the main sources of lead exposure. Despite the small amount of lead contained in these samples, lead consumption can have a considerable physiological impact [18]. Analytical methods that are extremely sensitive and accurate must be used to detect lead ions in water samples at trace levels [19]. This is what prompted the direct determination and separation of lead from aqueous solutions using the solid phase extraction method.

For selective extraction and separation of Pb(II) from real water samples, a new simple solid phase extraction technique based on a modification of SF@NPs with 8-AQ and 3-AQ via green microwave solvent-less technique.

2. Methodology
2.1. Materials and solutions

Silica fume (SF) was provided by the Ferrosilicon Company, Edfo, Egypt. In every experiment, double distilled water (DDW) was used. The appropriate amount of lead acetate salt was dissolved in DDW to prepare a stock solution of 0.1 M Pb(II). The required amount of salt was dissolved in DDW to prepare a 0.01M di sodium salt of ethylene diamine tetra acetic acid (Na_2EDTA) solution. 3-amino quinoline was of analytical grade and came from Merck. To support the pH values, Aldrich provided ACS reagent grade concentrated HCl and sodium hydroxide. Samples of Nile River water (NRW), drinking tap water (DTW), natural drinking water (NDW), groundwater (GW), and distilled water (DW) were collected from El-Minia City, Egypt.

2.2. Apparatus

Studies on solid-phase extraction were conducted utilizing the batch equilibrium method. The Accumet model 825 pH meter (Germany) was used to measure the pH. Sharp REM20 microwave oven (Korea) with 2.450 MHz microwave frequency with SF@NPs modification. FT-IR model 410 JASCO (Japan) was used to get the infrared spectra of SF@NPs and its modified phase both before and after modification. JSX-60 PA X-ray diffractometer by JEOL (Japan). Cu K radiation, Ni filtered (= 1.54184 A°), at 35 Kv and 15 mA, with a typical scanning speed of 2°/1 minute, within the range of 2 = 4°-100°, was used for the analysis. JSM-5400 LV JEOL (Japan) was used to obtain the scanning electron microscopy (SEM) analysis. Transmission electron microscopy (TEM) analysis was obtained using JSM-5400 LV JEOL (Japan). Model 75 mechanical wrist shaker (manufactured by Burrell Corporation

Pittsburgh. PA. U.S.A.). Atomic absorption measurements (AAS) were performed with Perkin-Elmer 2380 spectrometry (USA) to determine the quantiy of metal ions present in water samples. Every measurement was made at room temperature.

2.3. Modification of silica fume nanoparticles with quinoline derivatives using microwave technique

Before use, SF@NPs was properly cleaned with DDW and dried. Then, SF@NPs and its modified Nano adsorbent were irradiated to microwave radiation at a power of 20.0 W for 5.0 minutes in a glass watch. After being washed with DDW to remove any leftover quinolines and residue, the product SF@NPs loaded with 3AQ (SF-3AQ@NPs) was allowed to dry before use [2].

2.4. Batch equilibrium method

The batch equilibrium method was used to determine the adsorption capacity of Pb(II) from SF@NPs and its new modified phase (SF-3AQ@NPs), under static conditions. To a 0.5 mL of 0.1M Pb(II), 50.0 mg of each phase was added, and the total volume was completed to 50.0 ml by DDW at a pH range of 2.0 - 6.0 in a 100 mL measuring flask. 1.0 M HCl and 1.0 M NaOH solutions were used to adjust the pH. To achieve equilibrium, this mixture was mechanically shaken for 30 minutes with all prepared phases at room temperature. The unretained metal ion in the filtrate was evaluated by complexometric EDTA titration after the phases were separated by filtration and washed with DDW [2]. The same previous batch procedure was used to test and analyze the effects of other batch method parameters: shaking time, amount of adsorbent, and metal ion concentration. The following equation was used to determine the Pb(II) adsorption capacities (q_e) of the Nano adsorbents:

$$Pb(II) \, adsorption \, capacity \, (q_e) = \frac{C_o - C_e}{m} \times V \qquad mmol/g \qquad (1)$$

where: C_o refers to the initial concentration of Pb(II) (mmol/L), C_e refers to the equilibrium concentration of the unadsorbed Pb(II) in the decanted solution (mmol/L), and m refers to mass of the Nano adsorbent (g). The results obtained are the average of three replicates.

2.5. Application to real water samples

The performance of the novel nanocomposite adsorbent SF-3AQ@NPs was tested by evaluating Pb(II) concentration in real water samples including Nile River water (NRW), drinking tap water (DTW), natural drinking water (NDW), groundwater (GW), and distilled water (DW) before and after treatment with the novel adsorbents. Each water sample was taken and put into clean polyethylene bottles for storage. The analysis was performed after filtering NRW and GW. After adjusting the pH samples to the optimum pH value and shaking for 30 min, 50.0 mg of nanocomposite adsorbent (SF-3AQ@NPs) was treated with 50.0 mL of water sample spiked with 5.0 and 10.0 mg L^{-1} of Pb(II). Each filtrate was measured by AAS technique.

3. Results and Discussion
3.1. Characterization of the adsorbent
3.1.1. FT-IR

In order to explain chemical bonding, infrared spectral analysis has been used. It offers useful details about the compound's molecular structure and describes the change that has taken place as a result of the modification process. The main bands in IR spectrum of SF@NPs (Fig. 1a) could be seen

as follows: the strong band centered at 1105 cm^{-1} was attributed to the asymmetric stretching frequency of υ(Si–O–Si), the band centered at 799 cm^{-1} was due to symmetric stretching of υ(Si–O–Si), the band at 475 cm^{-1} was due to the bending frequency of υ(O–Si–O) and a broad and strong overlapped band at around 3436 cm^{-1} was due to υ(O–H) stretch [20]. Fig. 1c shows the modification of SF@NPs with 3AQ, the two bands at 3454 and 3326 cm^{-1} which attributed to asym. υ(NH$_2$) group and the band at 3192 cm^{-1} due to sym. NH$_2$ stretching were also decreased in length. A new band appeared in SF-3AQ@NPs at 3360 cm^{-1} which due to υ(H–bonded O–H stretch) as hydrogen bond was formed between 3AQ and SF@NPs. As happened before, the band of (Si–O–Si) appeared in SF-3AQ@NPs. According to the analysis of the FT-IR spectra, the strong band with a center at 1105 cm^{-1} that is attributed to the asymmetric stretching frequency of (Si-O-Si) in SF@NPs appeared in the spectrum of the modified Nano adsorbent, and the bands at the range of 900-675 cm^{-1} due to (C-H) "oop" bending disappeared and were replaced by the band at 475 cm^{-1}. The alteration of SF@NPs with 3AQ results in a powerful and stable adsorbent, which aided in the extraction and removal of Pb(II), Fig. 1d.
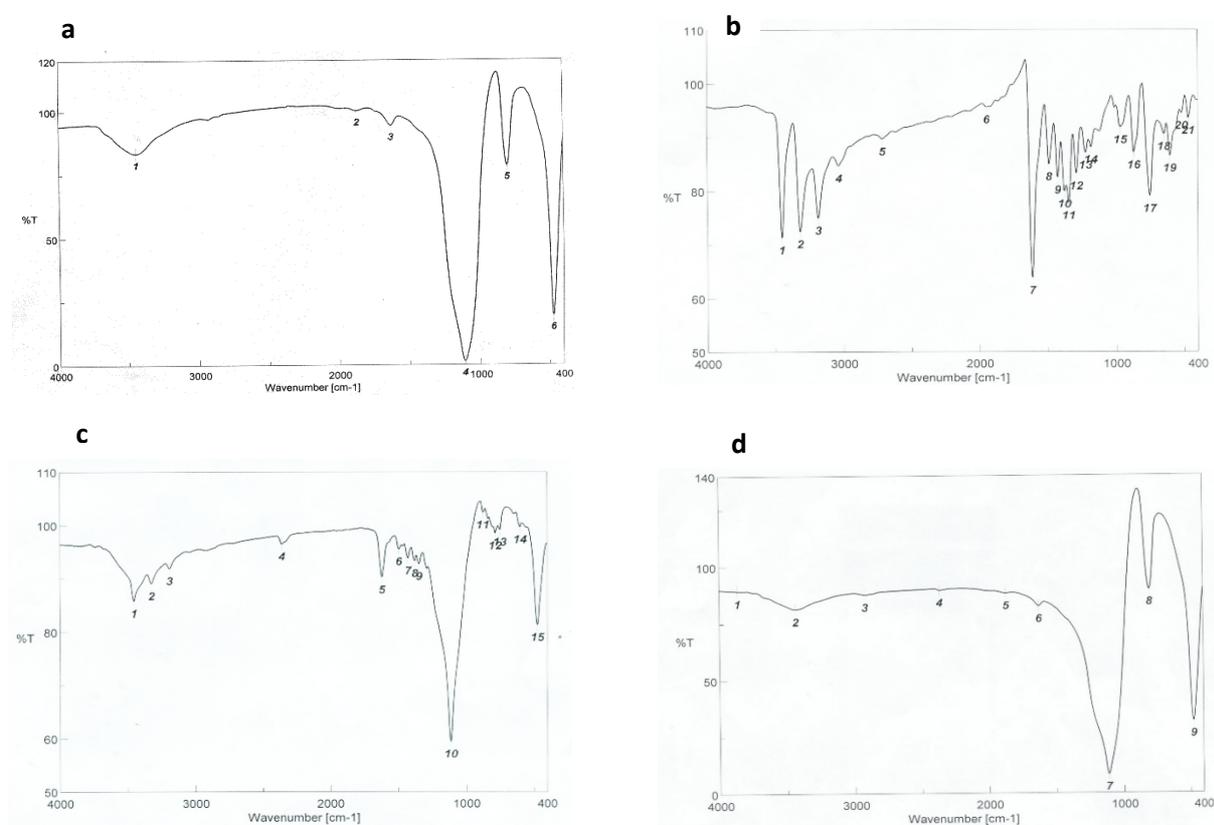

Figure 1: FT-IR spectra of Nano adsorbents: (a) SF@NPs (b) 3AQ, (c) SF-3AQ@NPs, and (d) SF-3AQ@NPs after adsorption of Pb(II).

3.1.2. XRD

The SF@NPs' X-ray diffraction pattern exhibits a significant hump in the range of 15-25 2Ө. This proves that the substance SF@NPs is amorphous silica [21] as illustrated in (Fig. 2a). XRD pattern of 3AQ (Fig. 2b) was sharp as they are crystalline materials. The XRD pattern of SF-3AQ@NPs shows that SF@NPs converted into sharp bands that are of crystalline 3AQ. This indicates the success of the modification of SF@NPs with 3AQ. It was evident from the X-ray diffraction spectra that the bands' strength increased after the SF@NPs were modified with quinoline derivative, Fig. 2c.
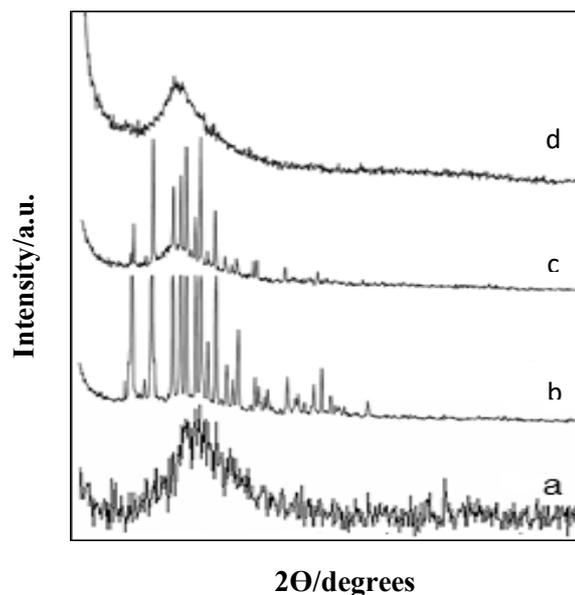
Figure 2: X-ray diffraction spectra of (a) SF@NPs, (b) 3AQ, (c) SF-3AQ@NPs, and (d) SF-3AQ@NPs after adsorption of Pb(II).

3.1.3. TEM

TEM analysis is an important tool used for studying the shape and particle size of materials. Fig. 3a and b show the TEM images of SF@NPS before and after modification with 3AQ. The SF@NPs is approximately spherical and has particles that are on average 0.157 microns in size, Fig. 3a. The particles are gathered after modification with 3AQ, and their sizes ranged from 0.113 to 0.185 microns, Fig. 3b. These results support the fact that SF and its modified phase is Nano adsorbents.

3.1.4. SEM

Before and after Pb(II) adsorption, the surface morphology of SF@NPs and its modified phase have been examined using scanning electron microscopy (SEM). In (Fig. 4a), the microphotographs reveal that SF particles are small in size and they are granuliform. In (Fig. 4b) SF-3AQ are also bigger and bigger than SF@NPs in size and shape, after adsorption of Pb(II), the particles became smallest which support the success of adsorption of Pb(II) by SF-3AQ@NPs, (Fig. 4c).
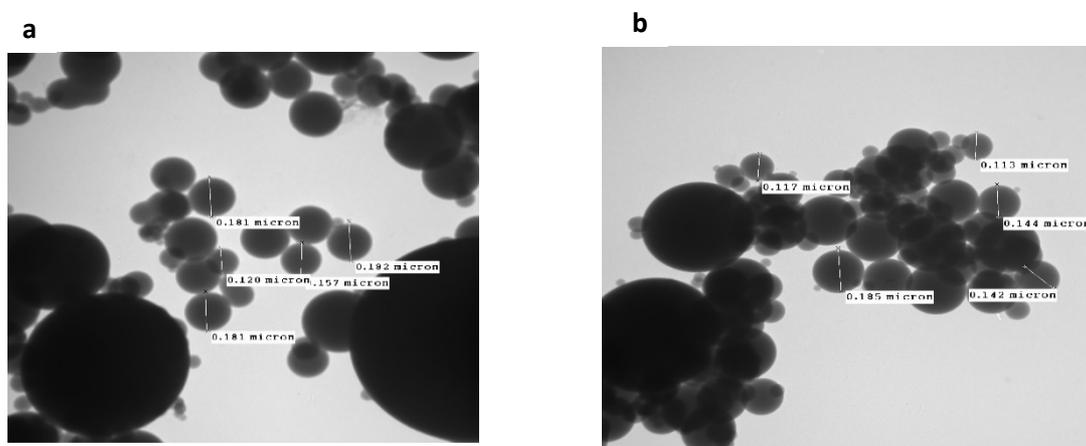

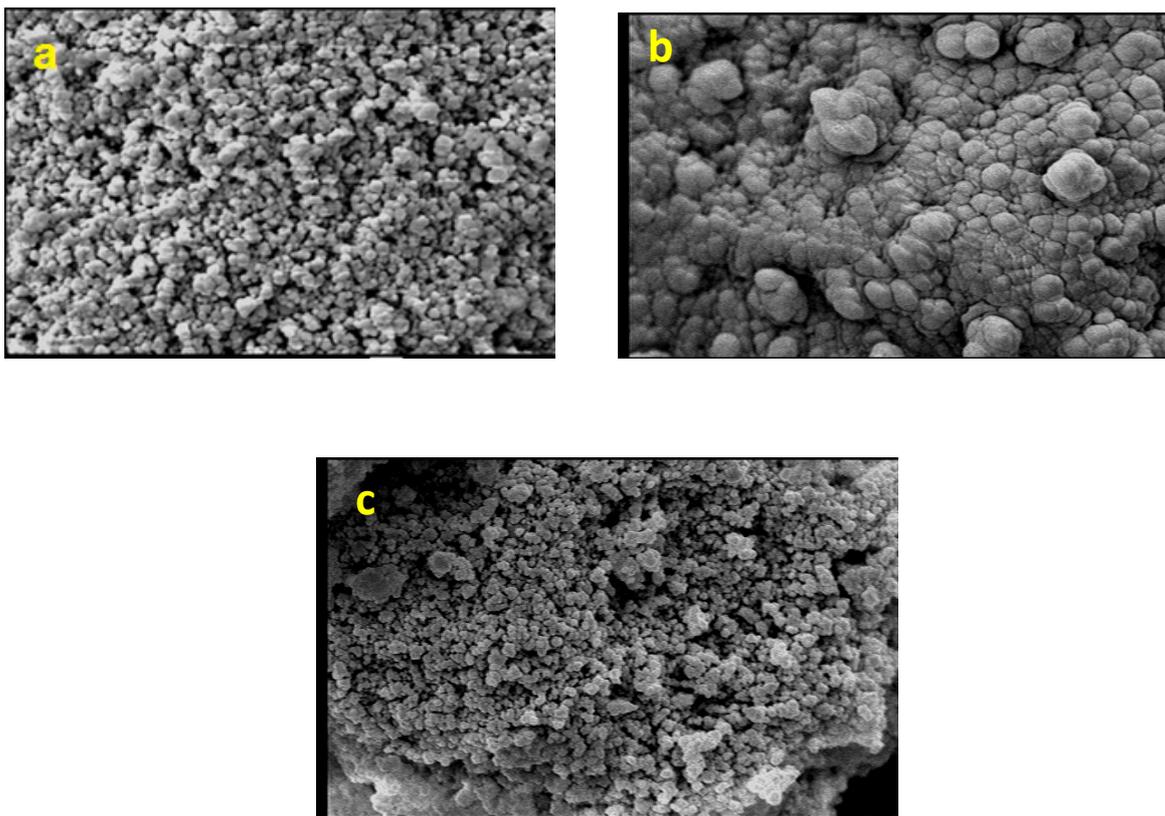**Figure 3:** TEM photographs of (a) SF@NPs and (b) SF-3AQ@NPs.

Figure 4: SEM photographs of (a) SF@NPs, (b) SF-3AQ@NPs, and (c) SF-3AQ@NPs after adsorption of Pb(II).

3.2. Adsorption study using the batch method

3.2.1 Microwave studies

Table 1 lists the specifics of the extraction modification conditions (power and time). This table clearly illustrates how microwave radiation synthesis provides a high extraction percentage with a rapid response time.

Table 1: The reaction conditions for the synthesis of SF-3AQ@NPs phase as a function of radiation power and time at a fixed mass ratio, 1g SF@NPs:1 g of 3AQ compound.

Power (Watt)	Time(min)	% Extraction	Adsorption capacity (mmol/g)
20	5	89.25	0.679
20	10	89.25	0.679
30	5	solidification	solidification
30	10	solidification	solidification

The extraction for the synthesis of SF-3AQ@NPs reached 89.25% with power 20W for 5 and 10 min, but increasing the power to 30W caused the adsorbent to solidify (m.p. =91-92 °C). The data in Table 1 allowed us to draw the conclusion that 20W for 5 min was the ideal power and duration for the microwave synthesis of SF-3AQ@NPs. Based on the findings from our analysis of the effects of the mass ratio of SF@NPs to the 3AQ compound, we chose the 1.0 g SF@NPs: 1.0 g 3AQ ratio as the optimum mass ratio for modification (Fig. 5).
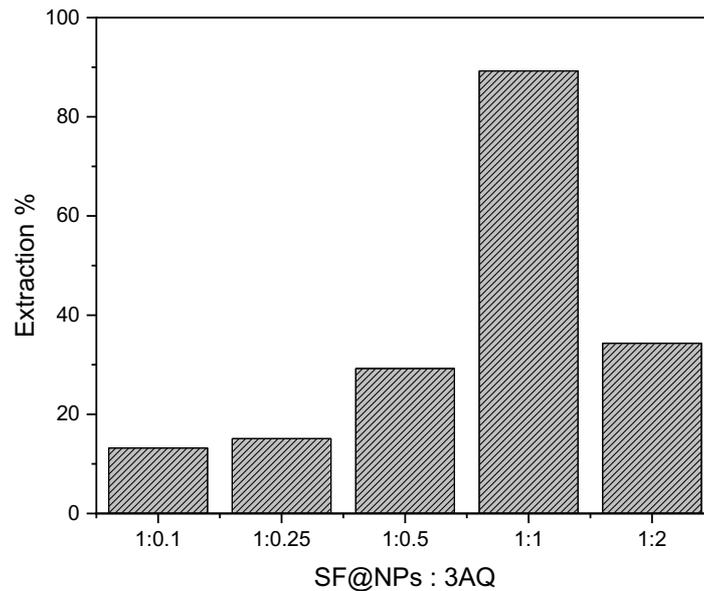
Figure 5: The extraction percent of the new modified SF@NPs composites for Pb(II) adsorption with different SF@NPs: 3AQ mass ratios

3.2.2. Effect of pH on metal extraction

The pH of the aqueous solution is a critical factor because it determines whether metal ions will be retained as metal ion-chelates on a solid phase material. In order to investigate the potential impact of reaction medium pH values on the observed metal adsorption capacity and extraction values, experiments were conducted in this section. This means that the model solution was used to study the impact of pH while holding all other variables constant in the pH ranges of 2.0 to 6.0. The extraction values for Pb(II) are displayed in (Fig. 6), which demonstrated that SF-3AQ@NPs were more able to remove lead than SF@NPs. Few amounts of lead can be adsorbed at low pHs (2.0 and 3.0), where the extraction of Pb(II) and adsorption capacity values are low and range from 0.0 to 0.114 mmol g^{-1}. As the pH rises to 6.0, Pb(II) extraction increases. This can be explained by the fact that, at low pH, the proton competes with metal ions for binding to the ligand, decreasing the extraction efficiency, whereas increasing the pH to 6 has been reported to have the tendency to retain understudy metal ions after their complexation. This is likely due to the dissociation of the sorbent functional group [22].
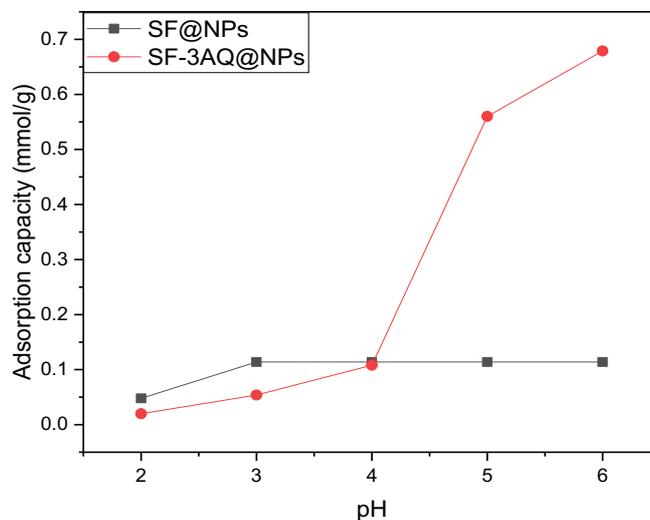

Figure 6: Effect of pH on Pb(II) adsorption capacity using SF@NPs and SF-3AQ@NPs adsorbents.

3.2.3. Effect of contact time

Batch adsorption experiments were carried out to investigate the impact of contact time on the removal of Pb(II) because contact time is a significant factor in the process of evaluating the adsorbent. The experiment was conducted utilizing a mechanical shaker at a time range from 5 to 60 min, a fixed sorbent mass of 50.0 mg, a fixed Pb(II) concentration of 0.05 mmol at a pH of (6.0), and a fixed contact solution volume of 50.0 mL. The highest Pb(II) adsorption for SF-3AQ@NPs requires the first fifteen minutes of shaking time, as illustrated in (Fig. 7). This demonstrated that SF@NPs modified with 3AQ produce effective Pb(II) extractants that take only a little time to complete the extraction process. This gives choosing the nanocomposite SF@NPS with 3AQ (SF-3AQ@NPs) for Pb(II) adsorption and removal a second benefit.
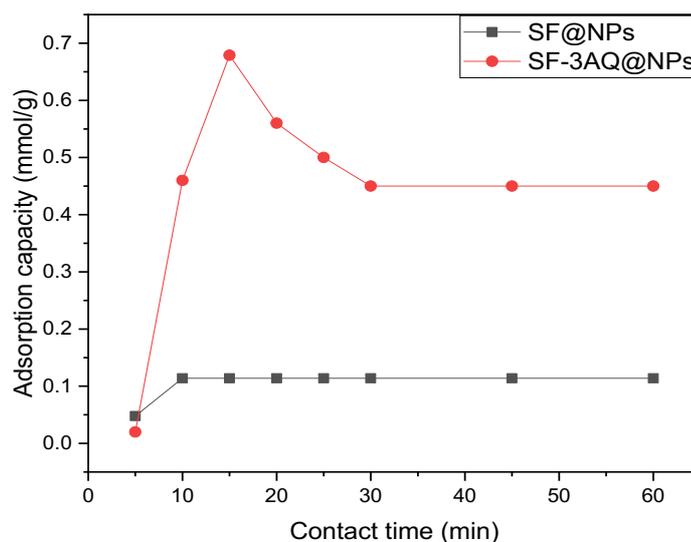

Figure 7: Effect of contact time on Pb(II) adsorption capacity using SF@NPs and SF-3AQ@NPs adsorbents.

3.2.4. Effect of adsorbent weight

The amount of adsorbent was maintained at the same levels for all other experimental parameters, including pH (5.0), starting concentration (0.05 mmol), and contact period (15 min). The adsorbent weight graph vs Pb(II) adsorbed per unit mass is shown in Fig. 8. The adsorbent weight ranged from 10.0 to 150.0 mg. The adsorption capacity of Pb(II) increased with increasing adsorbent weight until a constant value was attained, as can be shown. Previous results demonstrated that the maximum removal efficiency (= 89.25%) with SF-3AQ@NPs is due to the nature of 3AQ, which has a well-known chelating agent. This led to the decision to select it as the most effective one for the elimination of Pb (II) from water samples.

3.8. Application of Nano adsorbent for removal of Pb(II)

In order to verify the precision and accuracy of the new extraction method that has been proposed, the method validation should be looked at. Different concentrations (5.0 and 10.0 mg L^{-1}) of Pb(II) were spiked in various water samples to determine the procedure's accuracy. Pb(II) in all water samples was determined using by AAS technique. The results showed reasonable accuracy, reproducibility, and sensitivity, which are indicators of somewhat excellent analytical performance. Table 2 displayed the results that proved the reliability of the used new developed Nano composite adsorbent (SF-3AQ@NPs) for the detection of spiked ultra-trace levels of Pb(II) without matrix effect. As can be observed, recoveries of 99.4% to 100% were obtained, confirming the method's accuracy.
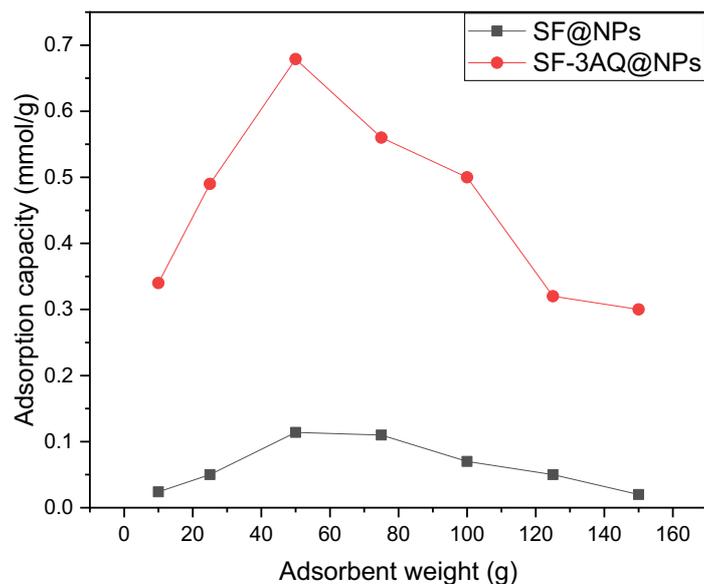
Figure 8: Effect of adsorbent weight on Pb(II) adsorption capacity using SF@NPs and SF-3AQ@NPs adsorbents.

Table 2: Results obtained for Pb(II) determination in various water samples after extraction by SF-3AQ@NPs adsorbent

Water sample	Spiked Pb(II) (mg/L)	Mass of the phase (mg)	Recovery[a] (%)
DW	5	50	100.0 ± 0.1
	10	50	100.0 ± 0.1
GW	5	50	99.73 ± 0.05
	10	50	99.69 ± 0.01
NRW	5	50	99.98 ± 0.1
	10	50	99.90 ± 0.5
DTW	5	50	100.0 ± 0.01
	10	50	99.56 ± 0.01
MDW	5	50	99.88 ± 0.1
	10	50	100.0 ± 0.05

[a] average of five determination ± standard deviation (S.D.)

4. Conclusion

For the extraction and removal of Pb(II) from an aqueous solution, a new Nano composite adsorbent (SF-3AQ@NPs) was created with a high percentage of 89.25%. It was used to remove Pb(II) with a high recovery value (99%), good accuracy, and no matrix interferences from natural water samples.

There is no conflict of interest.

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