Removal of Iron From Produced Water Using Silica Adsorbent Material

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A B S T R A C T

The removal of Iron from produced water using adsorbent materials is taking a space of attention from the perspective of researchers. In this work, the characterization of chemically modified silica used as Iron ions adsorbent using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), laser granularity instrument was performed. The point of zero charge (PZC) of modified silica was determined using titration method. Different parameters were used to better approach Iron removal. These parameters are 0.2 and 0.4 mg/l modified silica adsorbent dose, 30-180 min adsorption time and pH values of 4-10. The results showed that modified silica exhibited higher removal efficiency of Iron due to its surface characteristics. The results also showed that at 60 min adsorption time and pH 7, the maximum Iron removal efficiency with 99.99% and 99.98% was obtained using modified silica dose of 0.4 mg/l and 0.2 mg/l, respectively.

1. Introduction

Produced water (PW) generated from oil and gas production is the largest waste in the petroleum industry. It is contaminated with heavily immiscible oil and organics, heavy metals, salts, suspended solids, and radioactive components [1,2]. The volume of produced water in the world is approximately 200 Mbbl/d which constitutes three times the oil production [3]. The presence of heavy metal ions, even at extremely low concentrations in the produced water, has caused environmental problems [4]. The maximum concentration of Iron ions in water has been reported according to the World Health Organization to be 0.3 mg/l. If this excessive limit is exceeded it can cause blockage,

pipeline corrosion and environmental and biological hazards. Therefore, the Iron ions content should be reduced to less than 0.3 mg/l [5]. Depending on the chemical degree and mechanical emulsification, removing suspended Iron from the produced water can be a challenge in the treatment [6].

Adsorption is considered as a competitive technology for the purification and treatment of groundwater, wastewater, and industrial effluents. This process of separation may provide a cost-effective trade-off to combat water pollution. The principle of adsorption depends on whether the solid surface that comes into contact with liquids tends to accumulate a surface layer of solute molecules due to the imbalance of existing surface forces, increasing the need for adsorbents that can provide complex and effective abilities towards these metal ions [7].

The surface of silica adsorbent material is composed of oxygen atoms, and bonds confirmed on the tetrahedral part of silica and hydroxyl groups that bind to the specific edge of the silicate structure units. These useful groups provide superficial sites for metal ions. The surface of hydroxyl groups separates into natural water and acts as Lewis basics toward metal ions. The reaction of the metal surface bonding (adsorption) is usually preferred by metals due to the hydrolysis properties [8].

M. Valentukevičienė [9] studied application of natural silica adsorbent to remove ammonium and Iron ions from groundwater. They found that the Iron and ammonium removal efficiencies of 95% and 94% were achieved using silica sand. The ability of silica adsorbent to remove Iron and uranium ions from phosphoric acid was studied by El-Bayaa et al. [10] at different parameters such as adsorbent dose, adsorbate concentration, temperature and volume to weight ratio. They indicated that the maximum removal efficiency of Iron and uranium ions was 84% and 75%, respectively. Malekmohammadi et al. [11] found that silica can remove Iron appropriately, while zeolite is more suitable in removing ammonium and phosphate from water pollutants. They also found that activated carbon is effective in removing chemical oxygen demand contaminants. Thakuria et al. [12] found that groundwater contaminated with Iron and fluoride seriously affects health and the environment and adsorption and adsorptive filtration effectively remove them.

This study focuses on the removal of Iron from oil produced water by utilizing modified silica as adsorbent material under different parameters such as adsorbent dose, adsorption time and pH. The percentage of removal efficiency of Iron from produced water was also determined.

2. Experimental

I. Preparation of silica adsorbent

The chemical analysis of silica was performed using X-ray fluorescence (XRF) type (AMETEK) to be 99%. Silica was refluxed with 6M HCl for 4 hours and then washed with distilled water until it is acid free. The gel obtained was dissolved in 2.5 M NaOH followed by magnetic stirring for 6 hours. Drops of concentrated H_2SO_4 were added to the solution to obtain pH 8. The precipitate was washed with distilled water until it is base free and then dried in an oven.

The modified silica was characterized by Fourier transform infrared spectroscopy (FTIR) using the Bomen MB 100 model with KBr pellets in the range of 4000 to 500 cm-1. The surface morphology of modified silica was evaluated by Hitachi 3400N scanning electron microscopy (SEM). The particle size of modified silica was measured by Brookhaven 90 Plus laser granularity instrument. The particle size was determined three times for confirmation for each sample.

The determination of point of zero charge (PZC) of modified silica was carried out using electrolysis of aqueous solutions (blank solutions) with a pH changing from 1 to 11. A small amount (0.4 mg) of modified silica was added to these solutions and the aqueous suspensions were reached within 24 hours to equilibrium. The difference in pH, $\Delta pH = pH1 - pH2$, was determined using a digital pH meter where pH1 and pH2 are the initial and final pH of the solution, respectively. Therefore, point of zero charge was identified and corresponds to the lowest ΔpH [13].

II. Adsorption experiments

In the present study, the produced water was provided by the Petroleum Research and Development Center of the Middle Oil Company (East Baghdad). The Iron concentration and pH of produced water were 39 ppm and 6.6 respectively, determined using the inductively coupled plasma-optical emission spectrometry (ICP-OES) type Thermo Fisher iCAP 6500/USA with detection limit ≤ 0.01 μg/l and pH meter model Hanna Bench pH 211 Meter /UK sequentially. Optimal adsorption conditions were determined using specific experiments taking the effect of the adsorption time (30,

60, 90, 120, 150, and 180 min) and adsorbent dose (0.2 and 0.4 mg/l) at a constant pH of 7 and a temperature of 25 ºC.

The effect of the adsorption time of 30 min at different pH values (4, 7, and 10) on Iron removal efficiency was addressed.

During adsorption experiments, 0.2 mg of adsorbent was added into 1litter of the aqueous adsorbate solution using magnetic stirring at 50 rpm. The initial pH of the solution was adjusted by adding 0.1 *M* HCl and 0.1 *M* NaOH solutions to reach the desired pH value. After predetermined time period, 0.42 μm filter was used to separate directly the mixture of adsorbent and adsorbate. A sample of the filtered solution for Iron analysis was collected and analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES). The Iron removal efficiency (R %) was determined using the following expression [3].

$$R \% = (C_i - C_f)/C_i \times 100 \% \qquad\qquad (1)$$

Where *Ci* and *Cf* are initial and final concentration of Iron (ppm), respectively.

3. Results and Discussion

The FTIR spectrum of as received silica as shown in Figure 1 reveals that the peak positioned at 1078.67 cm^{-1} is usually related to the stretching vibration of Si-O from the siloxane (Si-O-Si) group. The peak positioned at 712.14 cm^{-1} is definitely related to the bending vibrations of Si-O-Si group, whereas the peak positioned at 607 cm^{-1} is attributed to the stretching vibrations of the Si-O-Si group. The FTIR spectrum of the modified silica as shown in Figure 2 shows that the peaks positioned at 2167.36 and 1619.48 cm^{-1} are related to the stretching and bending vibrations of the hydroxyl group, respectively. The peak positioned at 1078.67 cm^{-1} is usually the stretching vibration of Si-O from the siloxane (Si-O-Si) group. According to S. Rita et al. [14], the peaks positioned at 1030-1200 cm^{-1}are related to the stretching vibration of Si-O from the Si-O-Si group. The Si-O symmetry of Si-O-Si is certainly indicated by the peak positioned at 796.16 cm^{-1}. The peak at 800 cm^{-1} indicates the vibration of the Si-O symmetry of Si-O-Si. The peaks at 712.14 cm^{-1} and 607 cm^{-1} are related to the bending and stretching vibrations of the Si-O-Si groups, respectively.

From this, the peaks of the hydroxyl group and Si–O–Si indicate that these groups are responsible for adsorption of Iron ions onto the modified silica surface.
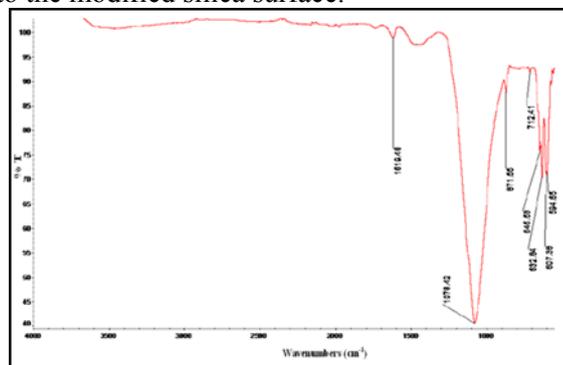

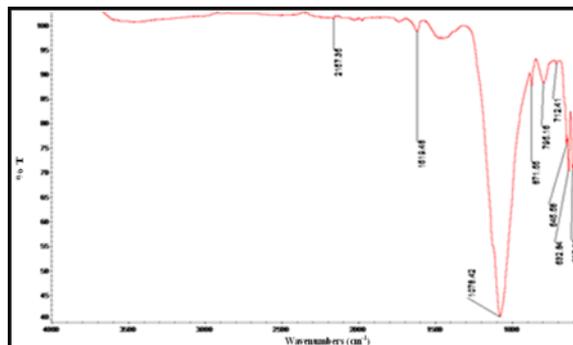**Figure 1: FTIR spectrum of silica as received**

Figure 2: FTIR spectrum of modified silica

SEM image of modified silica is shown in Figure 3. Obviously, modified silica prepared using chemical methods has irregular particles shape. Therefore, this structure can enhance the adsorption of modified silica for Iron ions. The particles size distribution and index of polydispersity are used to characterize modified silica. The term "polydispersity" or "dispersity" as recommended by international union of pure and applied chemistry analysis (IUPAC) is used to describe the degree of non-uniformity of size distribution of particles [15]. The particle size distribution of modified silica as shown in Figure 4 indicates that the average diameter is 1596.8 nm with a polydispersity index of 0.123.
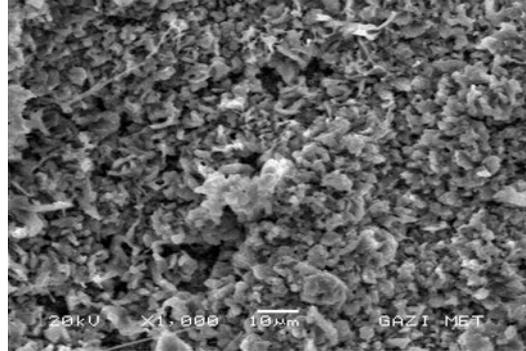

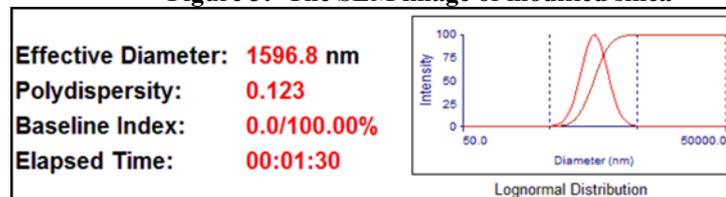**Figure 3: The SEM image of modified silica**

Figure 4: Particle size distribution of modified silica

The surface area of modified silica was calculated by nitrogen adsorption measurements initiated after gas leakage from the solid and application the Brunauer-Emmett-Teller (BET) equation. The surface area of silica and modified silica was determined with a value of 1.8 m^2/g and 9 m^2/g, respectively. Figure 5 illustrates the relationship between ΔpH versus pH_1 of modified silica which indicates that pH_{pzc} of modified silica is 3, due to the fact that the surface charge density of the suspension was set as zero. Modified silica is carried out a positive charge at pH value lower than 3. This is due to the low pH value in the comparison with the point of isoelectric or point of actually zero charges. When the pH is greater than 3, modified silica has a negative charge. The Iron ions in a solution with positive charges are attracted to the negatively surface charge of modified silica. From this, one would prefer a pH greater than pH_{pzc} for adsorption.
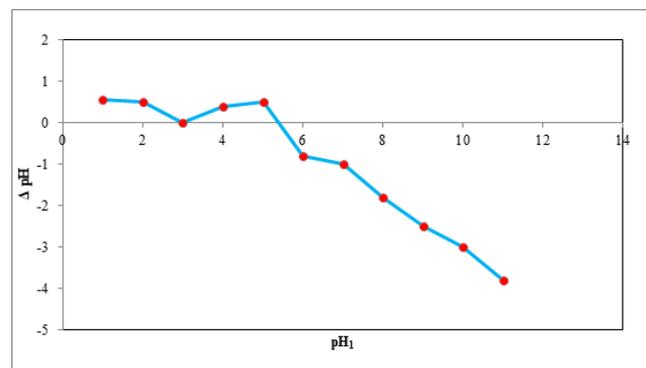

Figure 5: The relationship between ΔpH versus pH_1 of modified silica

The effect of pH on Iron removal efficiency is shown in Figure 6. The removal efficiencies of Iron ions were 44.67 %, 79.8 % and 12.6 % at pH of 4, 7 and 10, respectively, using adsorbent dose of 0.2 mg/l. Whereas, the removal efficiencies of Iron ions were 68.8 %, 91.7 % and 18.8 % at pH of 4, 7 and 10, respectively, using adsorbent dose of 0.4 mg/l for an adsorption time of 30 min. For an acidic solution at pH 4, the mechanism of adsorption is an active site only due to competition between Fe2+ and H+ ions on the surface of adsorbent. On the other hand, the positive charge of hydrogen ions associated with the modified silica surface stimulated the silica surface to have a positive charge;

therefore, the removal efficiency of Iron ions becomes low. At pH 7, despite the activation of Fe (OH)+ due to increased surface negative charge, maximum removal efficiency was obtained. This result is coincidentally with work of V. Orodu et al. [16] which indicates that maximum removal efficiency of heavy metals such as Fe(II) and Cd(II) ions from aqueous solutions obtained at pH 7 using snail shell adsorbent. At a pH of 10 represents the alkaline solution of produced water, a reduction in the removal of Iron ions occurred. This is due to the high solubility of silica at a pH greater than 9 and establishment of silicate anions. Therefore, one can conclude that preferred pH value for the best adsorption of all metal ions fall within 5 to7.
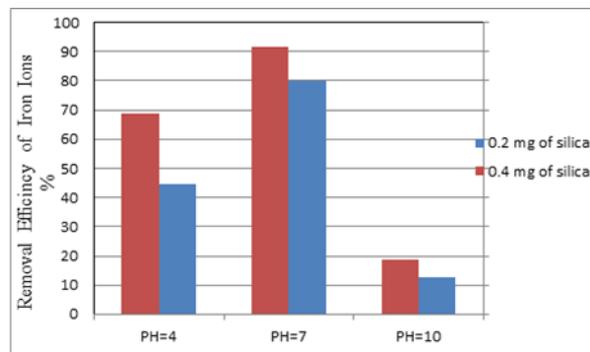

Figure 6: Effect of pH on the removal efficiency of Iron ions using different doses of modified silica

The Iron ions removal efficiency at pH 7 increases very rapidly up to 30 minutes as shown in Figure 7 which represents the relationship between adsorption time and Iron ions removal efficiency. It is clear from Figure 5 that the increase in adsorption time increased the removal efficiency of Iron ions. Iron ions removal efficiencies of 44.67% and 68.8% were obtained using an adsorption dose of 0.2 mg/l and 0.4 mg/l, respectively, with an adsorption time of 30 minutes due to the availability of vacant effective sites on the modified silica surface. The maximum Iron ions removal efficiency was reached to 99.99% and 99.98% using an adsorption dose of 0.4 mg/l and 0.2 mg/l, respectively, with an adsorption time of 60 minutes due to the large number of vacant active binding sites on the modified silica surface. From that, it is obvious that the adsorption is time dependent. Therefore, with the increase of the adsorption time, the removal efficiency of Iron ions inside the solution increased rapidly at first and then slowed down until it remained constant at the adsorption time of 60 minutes.
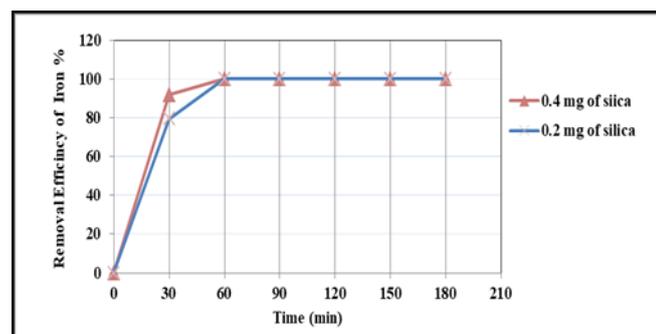

Figure 7: The removal efficiency of Iron ions versus adsorption time.

4. Conclusions

The modification of silica using chemical method is an attractive process due to less consuming time, low temperatures required and no requirements with aging is associated. The characterization of modified silica indicated that the peaks of the hydroxyl group and Si–O–Si were responsible for Iron ions adsorption. Moreover, the modified silica has a point of zero charge of 3 with an irregular particle shape with a surface area of 9 m^2/g compared to 1.8 m^2/g of the as received silica. The application of modified silica as adsorbent material to remove Iron ions from produced water was succeeded in reducing the Iron content from 39 to 0.00039 ppm. Therefore, one can conclude that chemically modified silica is an effective adsorbent material to remove Iron from produced water.

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