Modulation of Silica Gel Matrix by Glycine for Capturing Aqueous Iron(III) Ion: The Synchrotron X-ray Absorption

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Introduction

The major contaminants that could be found in water streams are organic and inorganic materials and biological organisms. The presence of heavy metals as pollutants in water is harmful to the human body, especially to the gastrointestinal tract and liver. Al-Anber et al. studied the sorption and removal of aqueous iron(III) ion and U(VI) ion using the silica gel functionalized tris(2-aminoethyl)amine moiety (SG-TAEA-NH_2). Among the most noticeable results are the successful sorption of Iron(III) or U(VI) ions that has been found with a maximum removal yield equal to ca. 98% (approx.) at a low concentration of metal ion

Objectives

The main objective is to prepare and characterize the modified Silica-Xerogel Matrix by Glycine entity through the sol-gel method. Afterward, the validity of new material toward the sorption of aqueous Fe(III) ion can be tested by a batch sorption technique. The mechanism and performance of hosting Fe(III) ion through the Sol-Gel matrix can be followed by the sorption isotherm and kinetics models invariant experimental parameters. recently, it has been reported that Glycine is found to play a role as a reducing agent (Joun Lee et al 2020). Therefore, we need to prove the oxidation state and the coordination environment of the iron ion within the SG and SG-Gly network via X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements

Synthesis

The silica gel (SG) matrix has been successfully modified by glycine (Gly) through the sol-gel method producing SG-Gly-Na+. The direct reaction of l,3-chloropropyltrimethoxysilane (CPTMS) with sodium glycinate (Gly-Na+) in a 1:1 molar ratio at 25 °C for 5 hours generates SG-Gly-Na+ as a white solid as shown in Figure 2.1-2.3. The new material has been characterized by ATR-FTIR, SEM, and elemental analysis.

Figure 2.3: SG-Gly^-Na^+ reaction.

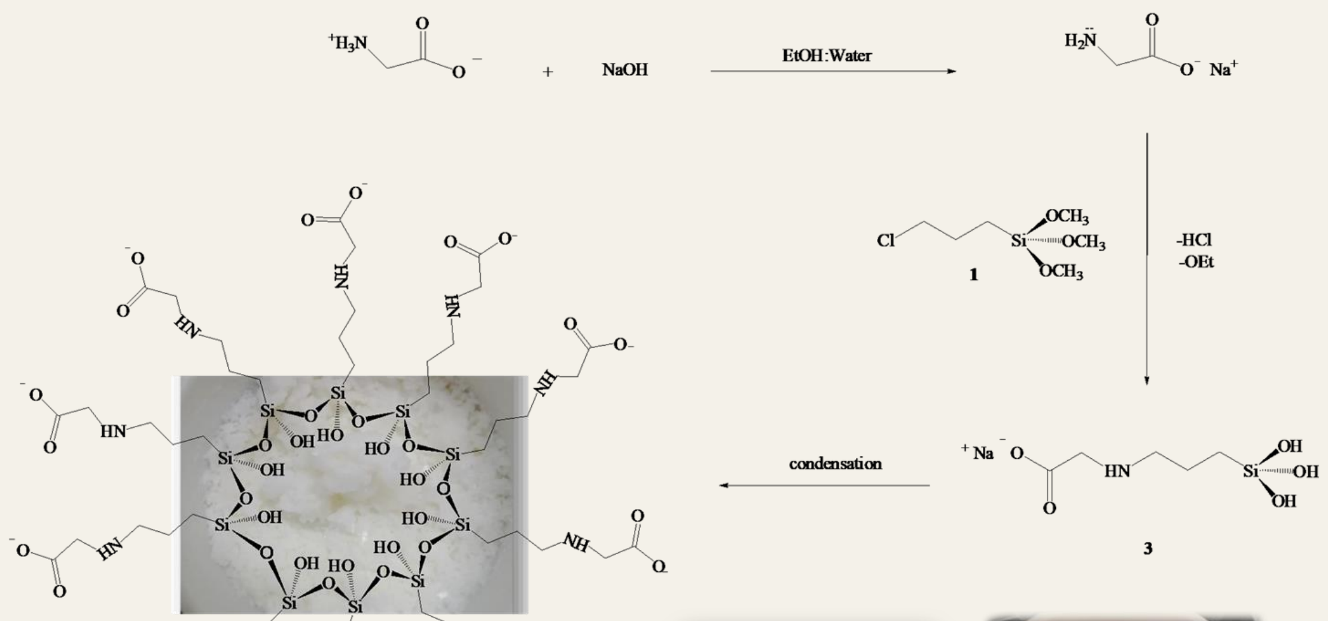

Fig. 2.2: Synthesis SG-Gly

Figure 2.1: The synthesized SG-Gly^-Na^+ material. **Figure 2.3**: The synthesized SG material.

Thermal Analysis

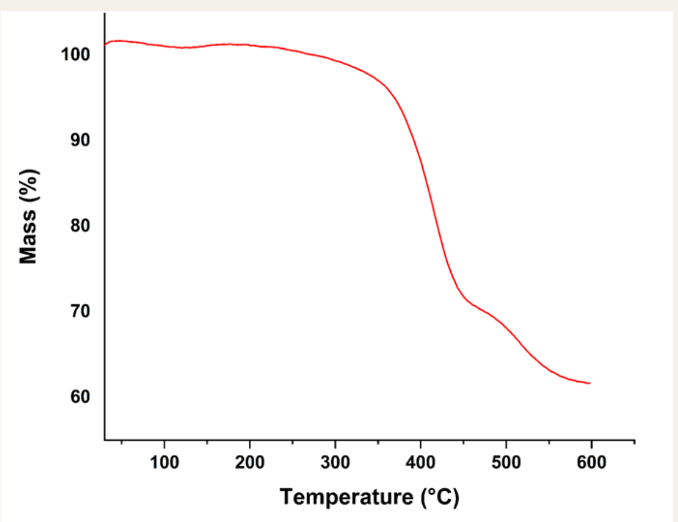

Figure 3.7 shows the Thermogravimetric analysis (TGA) curve of the prepared SG-Gly^-Na^+ material. In the TGA curves, there are two weight loss stages, viz., initial sharper weight loss below (350 – 450) °C and sharp weight loss between (450 – 550) °C. the first and the second weight loss is due to the carbonization or the combustion of organic entities (organic decomposition) due to the loss of carbon, hydrogen, nitrogen, and oxygen or CO_2 and NH_3. The total weight loss is less than 40 %. The thermal stability of these attached groups was thermally stable up to 350 °C.

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FTIR

The ATR and FT-IR spectra confirm the basic functional groups of Si-O-Si, Carboxylate, and secondary amine in the chemical structure of the new materials. The thermal analysis of TGA and DSC proves the thermal stability up to 350 C giving further evidence for forming a silica gel matrix including glycine entity.

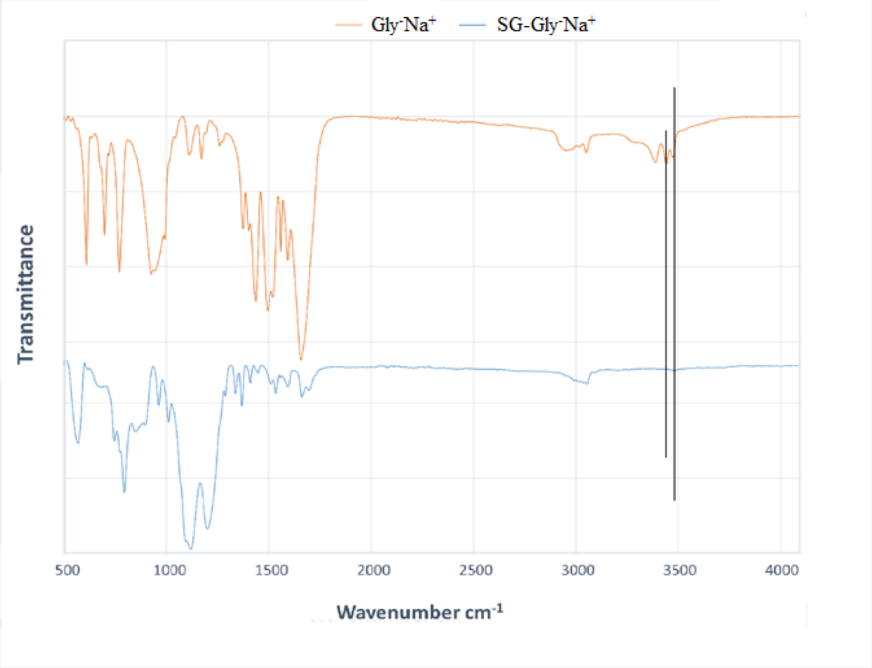


Figure 3.1: ATR-IR of Dry SG-Gly^-Na^+ with a comparison of Gly^-Na^+.

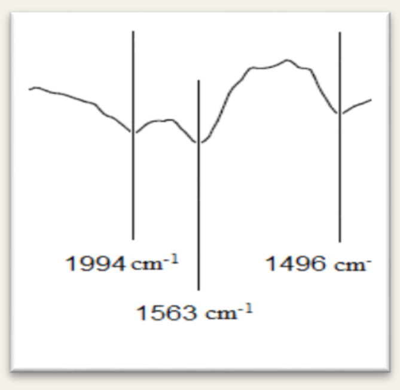
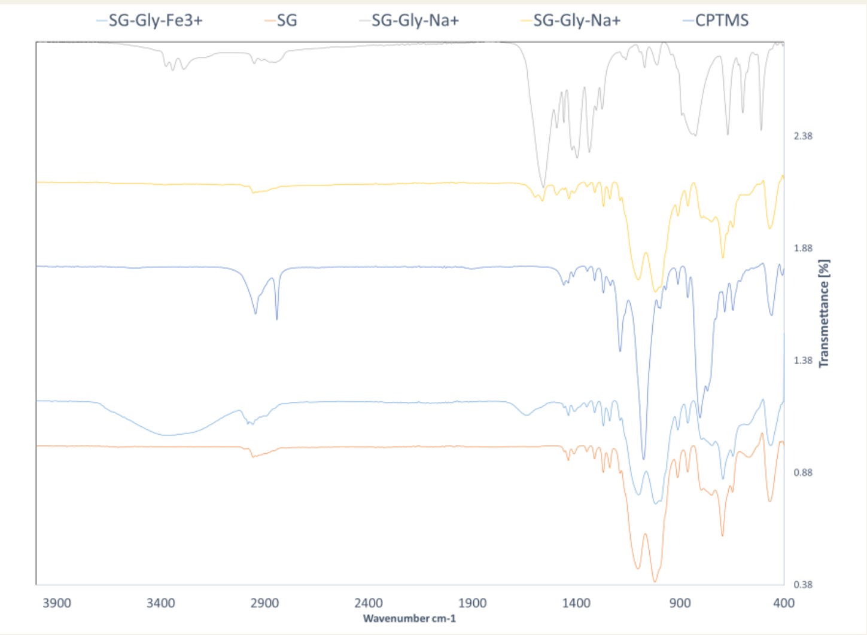


Figure 3.2: Enlarged image from ATR-IR of dry SG-Gly^-Na^+.



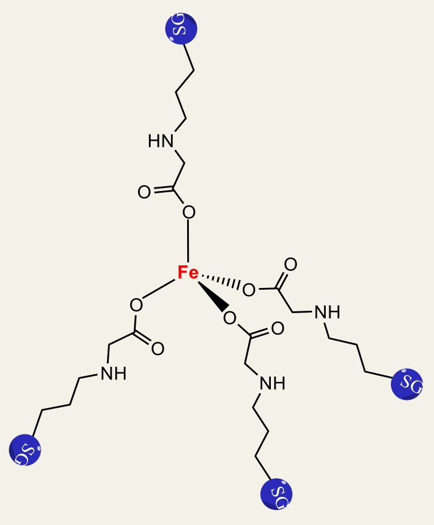


Figure 3.4: ATR-IR of wet water SG-Gly^-Na^+ and SG-Gly^-Fe^{+3}.

The X-ray diffraction

In general, the X-Ray Diffraction profile can be examined by studying the peak position, relative intensities (I/I◦), peak shape, and peak width. Here, it compares the surface shape of the prepared materials SG, SG-Gly-Na+ and its shape after the absorption of the Iron(III) ions (SG-Gly-Fe+3). Besides, a comparison with Gly-Fe+3 shows a Frankly change between them. As displayed by these p-XRD profiles, the samples (SG-Gly-Na+ and SG) were marked by the existence of a broad peak located at around 2θ = (21)° , which refers to amorphous silica, with amorphous carbon at 2θ = (7)° .

After modifying SG and Gly-Na+ as shown in figure 3.6. it shows that no new clear diffraction peak was observed except what exists in SG. However, some features indicate the imprinting of silica with glycine, such as a shoulder peak centered around 2θ = (30)° , which corresponds to the most intense diffraction peak Gly. also, there is a decrease in the intensity of peaks from (1681 and 1488) intensity unit (A.U) to (982.5 and 1097) (A.U), respectively. Besides, a change in its shape to be a broader and slight change in position as follows, 2θ = (7.380 and 21.22)° was shifted to 2θ = (7.06 and 21.76), respectively. The emergence of a new peak confirmed the sorption of Iron ions by SG-Gly-Na+ at 2θ = (14) , caused by the absorption of iron(III) ions, and the peak doubled to two peaks at 2θ = (20.78 and 21.18), which are similar to Gly-Fe+3 (Figure 4).

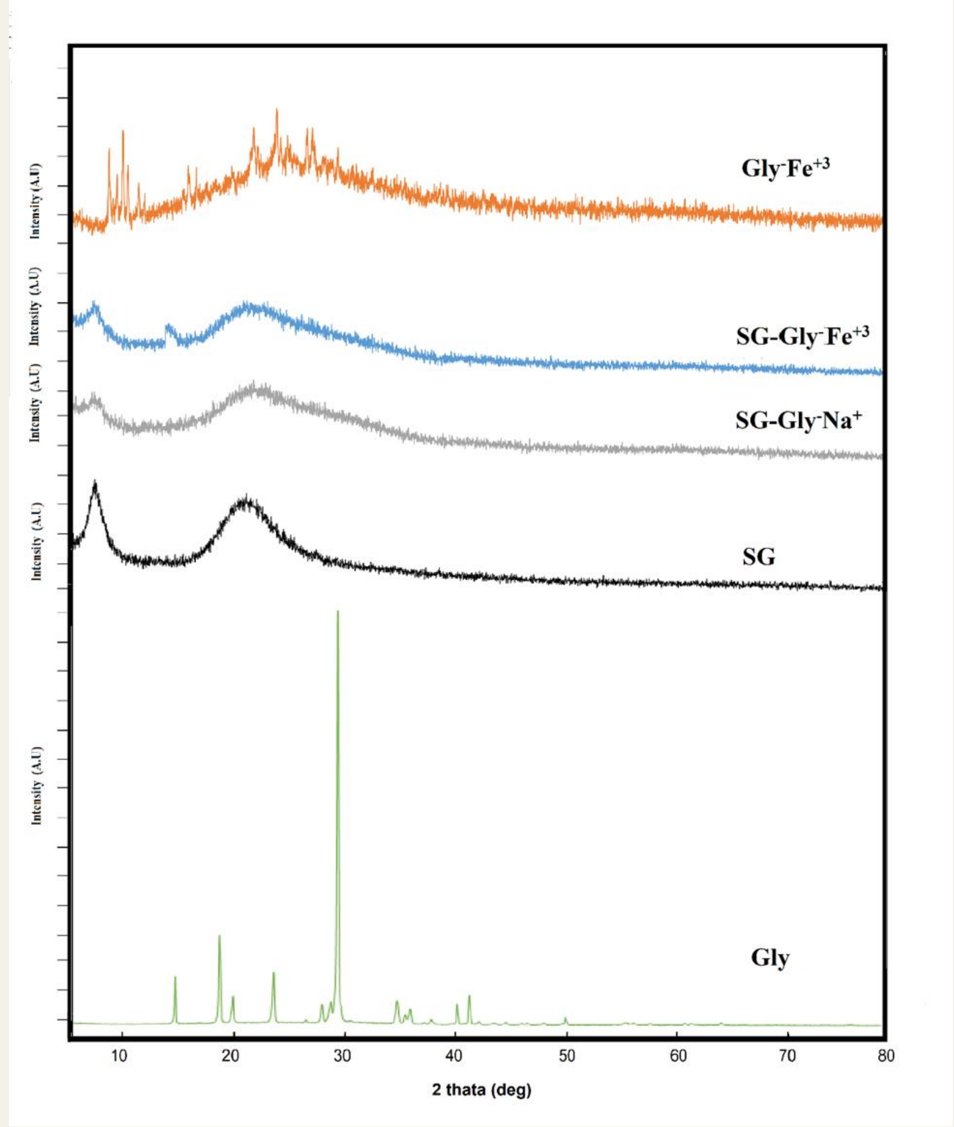
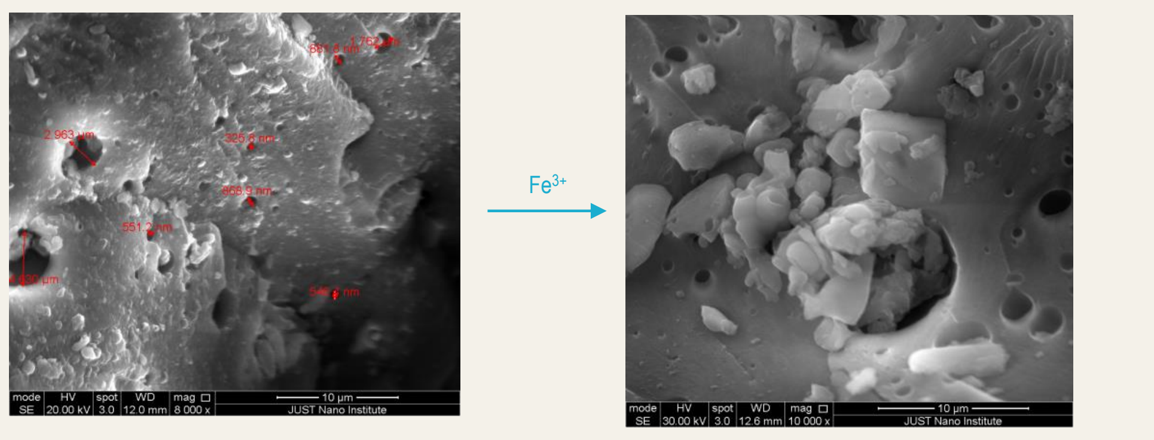


Fig. 4 The P-XRD of Gly and Gly-Fe3+ as well as the Silica Xerogel of SG, SG-Gly-Na+, SG-Gly-Fe3+.

Surface Morphology



Synchrotron X-ray Absorption

To determine the chemical state and coordination environment of Fe within SG at the atomic level, we performed X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements. To determine the Fe ion coordination, we compare the X-ray absorption near-edge structure (XANES) spectra of SG and SG-gly materials models, which has a symmetric Td coordination of Fe ions (Table 1).

All Fe samples exhibit a strong single pre-edge peak (7135 eV) initially comparable to SG-gly indicating Td symmetry. The absorption edge position in the X-ray absorption near-edge structure (XANES) spectra of SG-gly (7132 eV ev) moves slightly to a lower energy region compared to SG (7135 ev) (Fig. x), indicating a slightly lower oxidation state of the Fe species in the SG-gly. a weak pre-edge peak (7112 eV) appears clearly in the SG-gly spectrum more than in the case of SG. The lower intensity of the pre-and near-edge peak SG indicates the presence of monolayer coordinate Fe ions. it is known that Glycine was found to play a role as a reducing agent, which could not participate in reducing Fe(III) ion to Fe(0).

The peak at 7112 is a good indication of the presence of Fe(III) within the SG matrix. The Fe K-edge XANES profile for Fe in SG-gly and SG Figure x suggests the Fe single atoms might be in a Fe(III) valent state ($0 < \delta < +3$).

To our knowledge, this is the first report indicating the presence of Fe(III) in SG and SG-gly. As all the works reported before do not refer to any comments about the presence of Fe(III) on the surface of the adsorbents from the point of view of changing the oxidation number of the metal after adsorption.

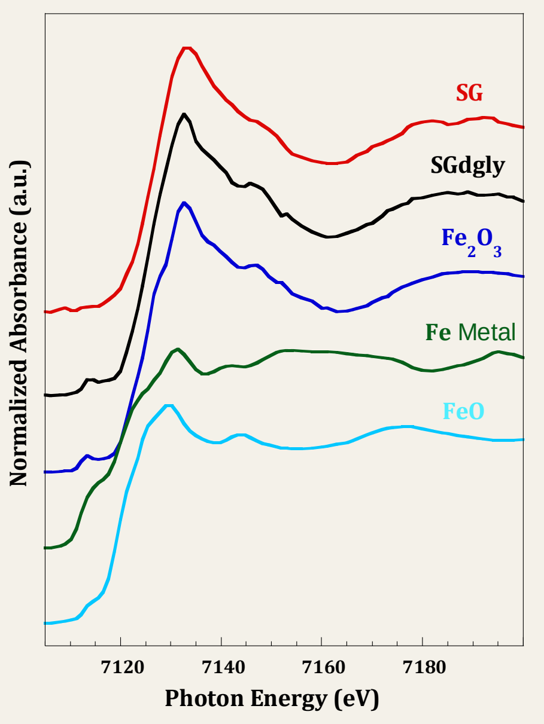


Fig.1 – XANES data collected at the Fe K-edge (7112 eV)

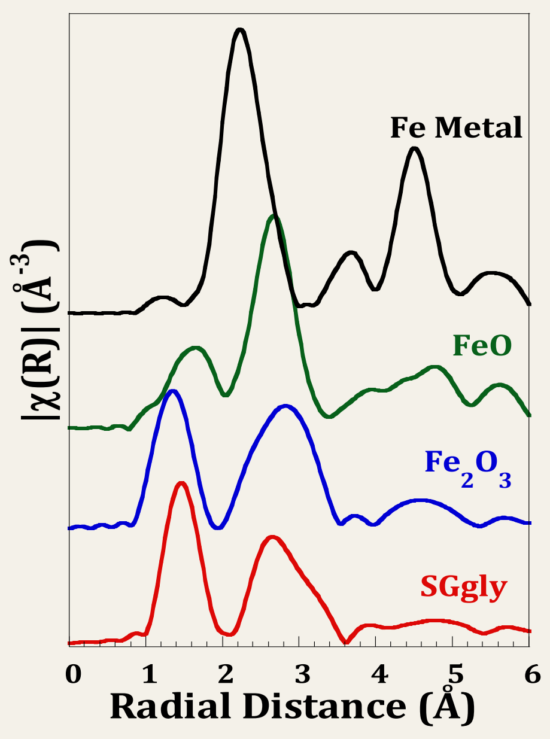
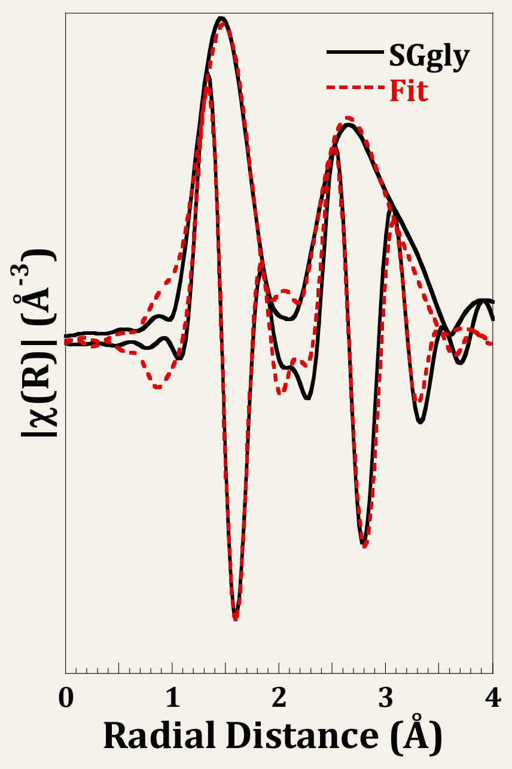


Fig.2 – Fourier Transform of the EXAFS signal collected at the Fe K-edge v



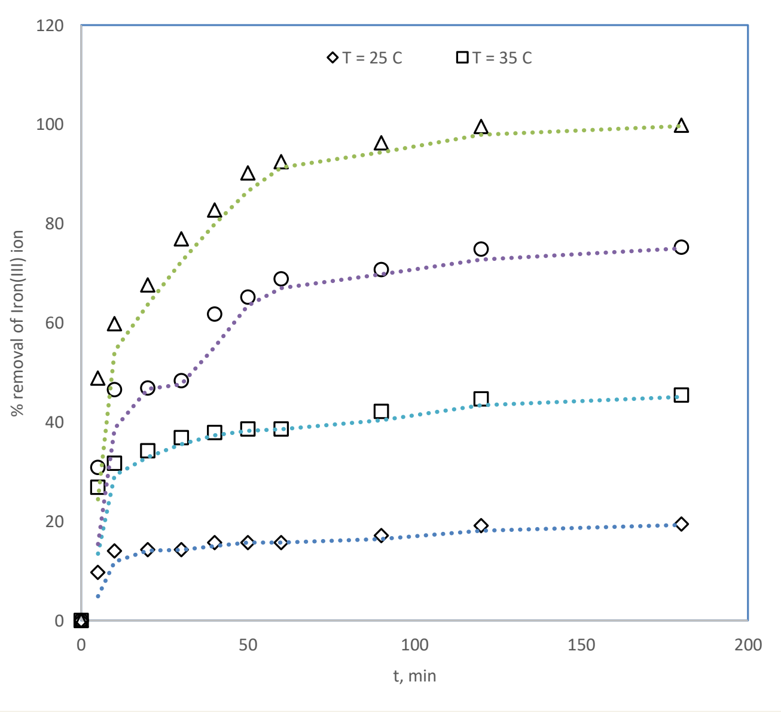


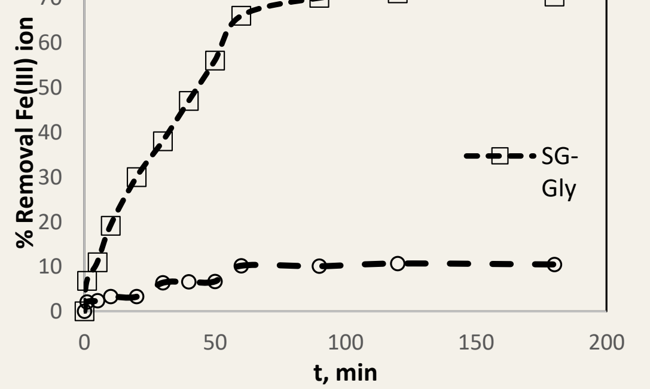
Fig.3 – Fitting the EXAFS data to derive the structural parameters

Tab.1 – EXAFS derived structural parameters around Fe central atoms

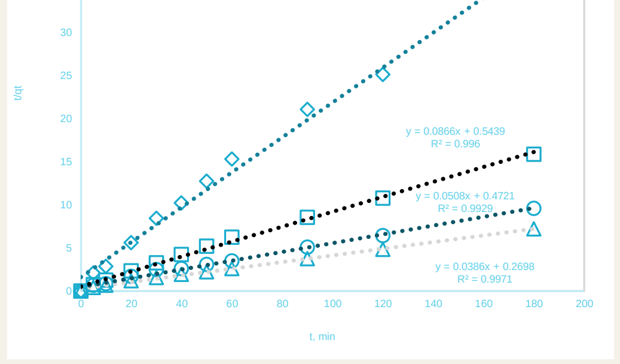
Sample	Bond	N (atoms)	R (Å)	σ^2 (Å²)	ΔE (eV)
SGgly	Fe-O	3.4±0.6	1.95 ± 0.003	0.0032±0.0005	-1.0±0.5
	Fe-Si	7.1±1.0	3.25±0.004	0.0071±0.0007	2.8± 0.4

Batch sorption of Fe (III) ion species

The new SG-Gly-Na+ material has been tested for the removal of iron(III) ion species from water through batch sorption. The Significance and efficiency of SG-Gly-Na+ toward Fe(III) ion is 90% in contrast to the SG.



Sorption of Fe3+ ion into SG-Cl vs SG-Gly-Na+ material, Ci = 100 mg L-1, T = 25 C, pHi = , 80 rpm, 2 g L-1, 100 – 250 m.



Pseudo-second order model for the sorption of Fe3+ ion into SG-Gly-Na+ material, Ci = 50 mg L-1, T = 25 - 55 C, 80 rpm, 2 g L-1, 100 – 250 m, pHi = 5.0.

Conclusion

It shows that the modification of SG with GlyNa+ could enhance the sorption of Fe3+ ions by 70 % in contrast with SG-Cl (10 %). Recently it has been reported that Glycine is found to play a role as a reducing agent (Joun Lee et al 2020). Herein, it is found that no significant effect for the reducing Fe(III) ion → Fe(0) within the network of the SG-Gly is observed based on the Synchrotron X-ray Absorption: EXAFS & XANES.

References:

1- Joun Lee et al 2020 Nanotechnology 31 455601
2- Zaitoun, M., Al-Anber, M., and Al Momani, I., 2019. International Journal of Environmental Analytical Chemistry, 100(13): 1446-1467.
3- Mohammed A. Al-Anber, Idrees F. Al-Momani, Mohammed A. Zaitoun, Wala' Al-Qaisi. Journal of Radioanalytical and Nuclear Chemistry (2020) 325:605–623
4- Al-Anber, M.A., Al-Adaileh, N., Al-Momani, I.F., Al-Anber, Z. , Journal of Radioanalytical and Nuclear Chemistry, 329 (2021) 865-887.