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Nitrite Removal from Lake Urmia Sediments Using Biohydrogel Based on Isolated Soy Protein/Tragacanth/ Mesoporous Silica Nanoparticles

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Abstract

Lake Urmia is one of the largest saltwater lakes in the world. In recent years, due to the drought conditions and the uncontrolled entry of industrial wastewater into the lake, the amount of some chemical pollutants has been increased dramatically in lake sediments. The most important pollutants in the lake are chemical organic compounds, heavy metals, nitrate, nitrite, among which, nitrite pollution is very important. The aim of this study was to prepare and asses the efficiency of a biodegradable biohydrogel based on isolated soy protein/tragacanth containing mesoporous silica nanoparticles and lycopene pigment (ISP/ TG/MPS/Lyc) in removal of the nitrite from the Lake sediments. The physicochemical characteristics and structure of the biohydrogel are investigated by scanning electron microscopy, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction, and thermal gravimetry analysis (TGA) techniques. Five optimal biohydrogels including pure ISP, ISP/TG, ISP/MPS, ISP/Lyc, and ISP/ TG/MPS/Lyc are used for chemical treatment of Lake Urmia sediments. For this purpose, biochemical oxygen demand (BOD), chemical oxygen demand (COD), and nitrite of sediments are examined before and after treatment with biohydrogels. According to the FTIR results, there is only physical interaction between lycopene and isolated soy protein. According to the TGA results, adding silica mesoporous to biohydrogel increases its thermal stability. Tragacanth gum and lycopene pigment reduce water solubility and increase the WAC of biohydrogel. The biohydrogel significantly reduces the BOD and COD of the sediments. The biohydrogel reduces nitrite content up to 90%, while reducing nitrate content by almost 30%. The results show that the biohydrogel containing lycopene selectively purifies nitrite from the sediment solution of Lake Urmia.

Key words: Lake Urmia, Nitrite removal, Biohydrogel, Sediment pollution

1. Introduction

Lake Urmia is one of the largest saltwater lakes in the world. In recent years, due to the drought conditions and the uncontrolled entry of industrial wastewater into the lake, the amount of some chemical ions and oxygen in the lake has changed dramatically. The most important pollutants in the lake are chemical organic compounds, heavy metals, nitrate, nitrite, biochemical oxygen demand (BOD), and chemical oxygen demand (COD), among which, nitrite pollutant is very important [1, 2].
Biohydrogel is made up of biological macromolecules made up of a large number of small, similar subunits that are joined together by acovalent bond to form a long chain. Biohydrogels, like synthetic hydrogels, have the ability to absorb large amounts of water. In the normal course, biohydrogel or macromolecules are intracellular compounds that enable the organism to survive in harsh environmental conditions. The biopolymer materials are reversible to the environment unlike

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petroleum polymers and they do not pollute the environment [3]. Soy protein isolate contains at least 90% protein, which is extracted from soybean meal by removing fat and carbohydrates. The use of isolated soy protein (ISP) in various industries is due to increasing the protein content of the product, high water absorption, and emulsifier properties of isolated soy protein. Isolated soy protein has a high water absorption capacity (WAC) and can act as a biohydrogel [4].
Tragacanth is the secretion of dried gum fromseveral plant species. Tragacanth gum (TG) is extracted from the stem by mechanical activity. Tragacanth contains 10–15% water, 3–4% minerals, and 3% starch. Tragacanth is composed of galacturonic acid, which binds to galactose and xylose sugars. Tragacanth easily absorbs the water and forms a gel in the presence of water, and due to the adhesive properties of tragacanth, it can be used to increase the physical resistance of biohydrogels.[5, 6] Nanoparticles have been considered in various industries such as filtration, electronics, and polymer industries due to their various applications. Mesoporous silica is solid materials that have porous like honeycomb pores with hundreds of empty channels that are capable of absorbing and encapsulating relatively large amounts of bioactive molecules. Prominent features of mesoporous include high surface area, adjustable size, and good chemical and thermal stability. Scattered colloidal systems containing dispersed silica particles are used in various industries, including catalysts and biopolymers [7]. Lycopene (Lyc) is a powerful antioxidant that can help human body protect against degenerative diseases. This is done by neutralizing free radicals in the body. Lycopene can help with DNA damage in cells as well as better cell function. This pigment can easily react with nitrate and nitrite oxides and remove them from the environment [8].
In this study, isolated soy protein/tragacanth modified with nanoparticles of mesoporous silica and lycopene was used to reduce BOC, COD, and nitrite. In the first part of this study, the physicochemical and mechanical properties of ISP/ TG/MPS/Lyc biohydrogel were investigated using techniquesn such as infrared spectroscopy and scanning electron microscopy (SEM). In the second part, the ISP/TG/MPS/Lyc biohydrogels were used to remove nitrite from Lake Urmia sediments and the efficiency of reducing pollutants was investigated.

2. Materials and Method

Isolated soy protein (with more than 90% protein) was produced by Crown China. Tragacanth was as-obtained from the Medicinal Plants Store (Urmia, Iran). Mesoporous silica nanoparticles (with a particle size of 30–100 nm) were produced by Nanogilosuzak Company (Iran, Tehran). Lycopene powder (with red appearance and product code 8-65-502) was purchased from the Iran Chem Book Co (Iran, Tehran). 2,2-diphenyl-1-picrylhydrazyl (DPPH), magnesium nitrate, calcium chloride, and other chemical compounds used were purchased from Merck (Germany) and Sigma-Aldrich (USA).
To prepare biohydrogel, isolated soy protein powder was dissolved in 100 mL of water at 70 °C by a magnetic stirrer (RS3001, MLW, Germany) at 2000 rpm. The pH of the solution was then adjusted to 10 using NaOH solution (0.1 N). Then, tragacanth powder was added to the solution and dissolved at a temperature of 70 °C by mechanical stirrer (BH8, Iran) at a speed of 1500 rpm for 1 h. Glycerol (as plasticizer) was then added to the solution as a 40% by weight of dry matter and dissolved in the solution for 20 min under the same conditions. Then, the mesoporous silica powder was added to the solution and dispersed by a mechanical mixer at 1500 rpm for 1 h. Finally, lycopene powder was added to the solution and dispersed by a mechanical mixer at 1500 rpm for 1 h and a gel-like solution was formed. 25 mL of the prepared final gel (including soy protein isolate, tragacanth, silica, and lycopene) was poured into special plates with a diameter of 10 cm

and dried for 48 h at room temperature. Different properties of the prepared biohydrogel such as soulobility in water, moisture content, water absorption capacity, and antioxidant activity were determined by standard methods.
In the next section, the biohydrogel was used to reduce the pollution of Lake Urmia sediments. To treat lake sediments with biohydrogel and to evaluate the efficiency of pollution reduction, sediments of different parts of the lake were sampled. 20 g of lake sediments were dispersed in 100 mL of distilled water and stirred with a mixer for 1 h. The water was then separated from the solids by passing through a strainer. Separated water was poured into the beaker and 5 g of biohydrogel was placed inside it and it was shaken for several hours with a balloon shaker (TM52E, Iran). After treatment of the sediment solution with biohydrogel, the biohydrogel was separated from the solution. The chemical properties of the sediment solution (BOD, COD, nitrate, and nitrite) were analyzed before and after treatment with biohydrogel and the pollutant removal efficiency (PRE) was calculated.

3. Results

3.1. Biohydrogel properties

Figure 1 shows the 3D curve of the effect of the isolated soy protein: tragacanth gum ratio, silica mesoporous nanoparticles concentration, and lycopene concentration on solubility, moisture content, water absorption capacity, and antioxidant properties. As can be seen from the 3D curves, the addition of tragacanth gum, MPS, and lycopene reduces the solubility of biohydrogel in water. The most effective in reducing water solubility has been MPS, followed by lycopene and tragacanth. Because lycopene pigments are insoluble in water, a reduction in solubility was expected due to increased lycopene. Mesoporous silica nanoparticles are waterproof naturally and can reduce the solubility by being placed between isolated polymer chains of soy protein and increasing its structural strength. In the structure of tragacanth, there is a substance called tragacanth (bassorin), which is insoluble in water, which reduces the solubility of biohydrogel in water. The curve of moisture content and water absorption capacity shows that MPS does not have much effect on the moisture content of biohydrogel and water absorption capacity and only slightly increases the moisture content and water absorption capacity, which is probably due to the presence of cavities. In its structure, it has the ability to trap water molecules. Lycopene reduces moisture content and water absorption capacity. Due to the fact that this pigment is hydrophobic, the presence of lycopene molecules in the biohydrogel structure reduces the presence of water molecules. The presence of tragacanth gum in the biohydrogel structure has increased the moisture content and water absorption capacity. Due to the fact that tragacanth is a compound that strongly absorbs water and has a gel-like property, an increase in the percentage of moisture and water absorption capacity in the presence of tragacanth was expected. In general, the presence of MPS and tragacanth increases the percentage of moisture and water absorption capacity by creating vacant spaces in the biohydrogel structure and creating gel-like properties. Montazer et al. prepared the tragacanthsilver gum hydrogel and examined its moisture and adsorption properties, the results of which confirm the results of the present study [9]. The results of the present study are in line with the research of Hosseini et al [10].
The curve of the antioxidant properties of biohydrogel shows that tragacanth does not have a significant effect on antioxidant properties, but MPS has greatly increased the antioxidant properties of biohydrogel. In general, silica nanoparticles have the ability to physically absorb free radicals, which is why they cause these radicals to go out. The mesoporous silica nanoparticles also

have the ability to disable radicals due to their very high surface-to-volume ratios. Lycopene is a member of the carotenoid family of phytochemicals and a natural pigment that, unlike other carotenoids, is not converted to vitamin A. This pigment has a very high antioxidant property, so the antioxidant properties of biohydrogel are greatly increased in the presence of lycopene.

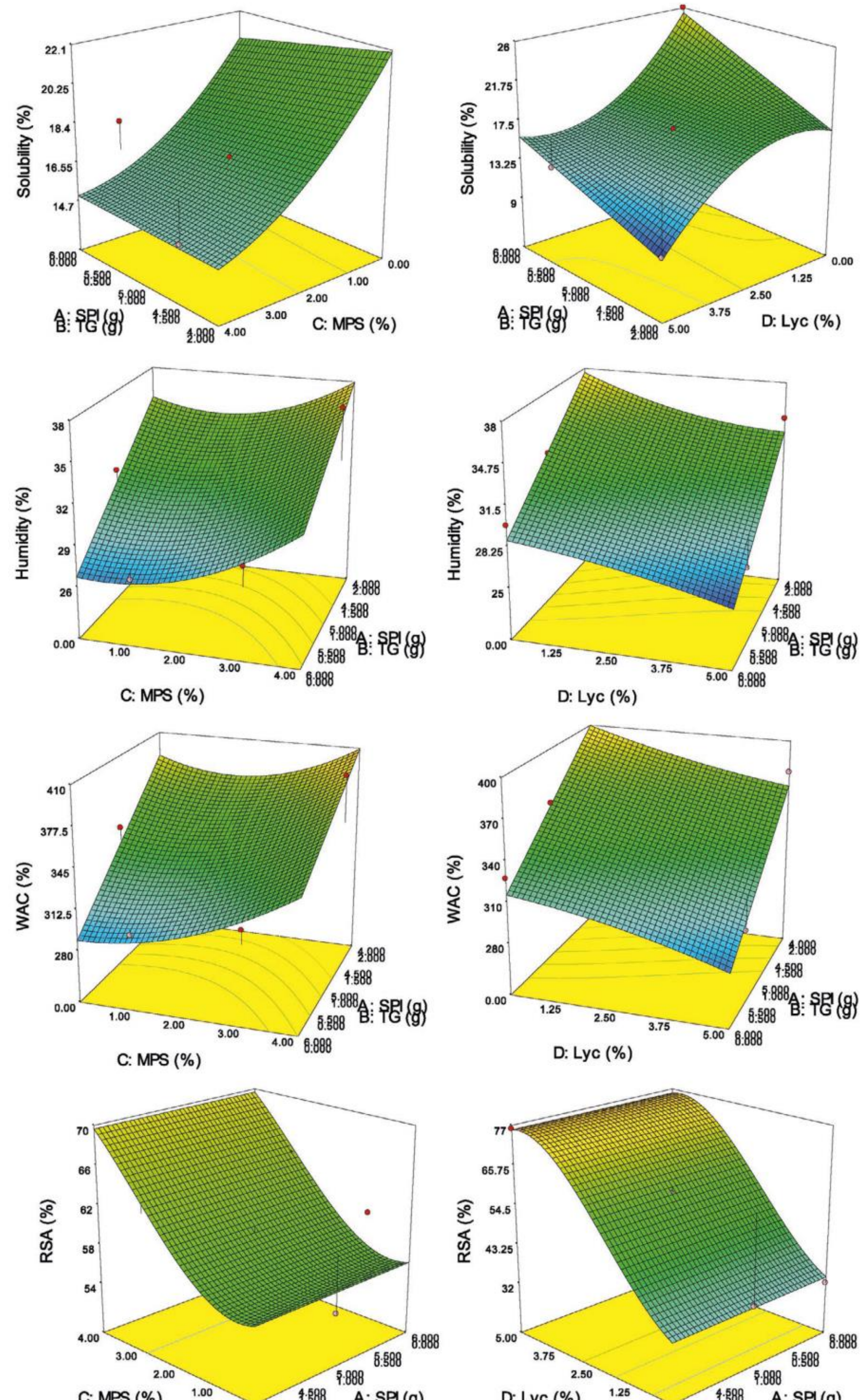

Figure 1. 3D curve of the effect of independent factors on solubility, humidity, WAC, and RSA of ISP biohydrogels

3.2. SEM, FTIR and XRD Tests

Figure 2 shows SEM images and FTIR spectra of ISP biohydrogels. As can be seen from the SEM images, pure ISP biohydrogel has a smooth, uniform, nonslit surface, while ISP/TG biohydrogel surface has a slit, which may be due to the gel properties of tragacanth, which increases the moisture content of the biohydrogel and has caused a gap at the level of the biohydrogel. In the ISP/MPS biohydrogel, small gaps are seen on the biohydrogel surface, and also the MPS nanoparticles are distributed nonuniformly in the biohydrogel. The size of these nanoparticles in some areas is between 20 and 100 nm, while in other areas, the size of the particles is larger, due to the accumulation of particles. In the ISP/TG/MPS/Lyc biohydrogel, due to the presence of tragacanth, MPS and lycopene, as well as nonuniform distribution of MPS nanoparticles in the biohydrogel the cracks are observed in the biohydrogel structure.

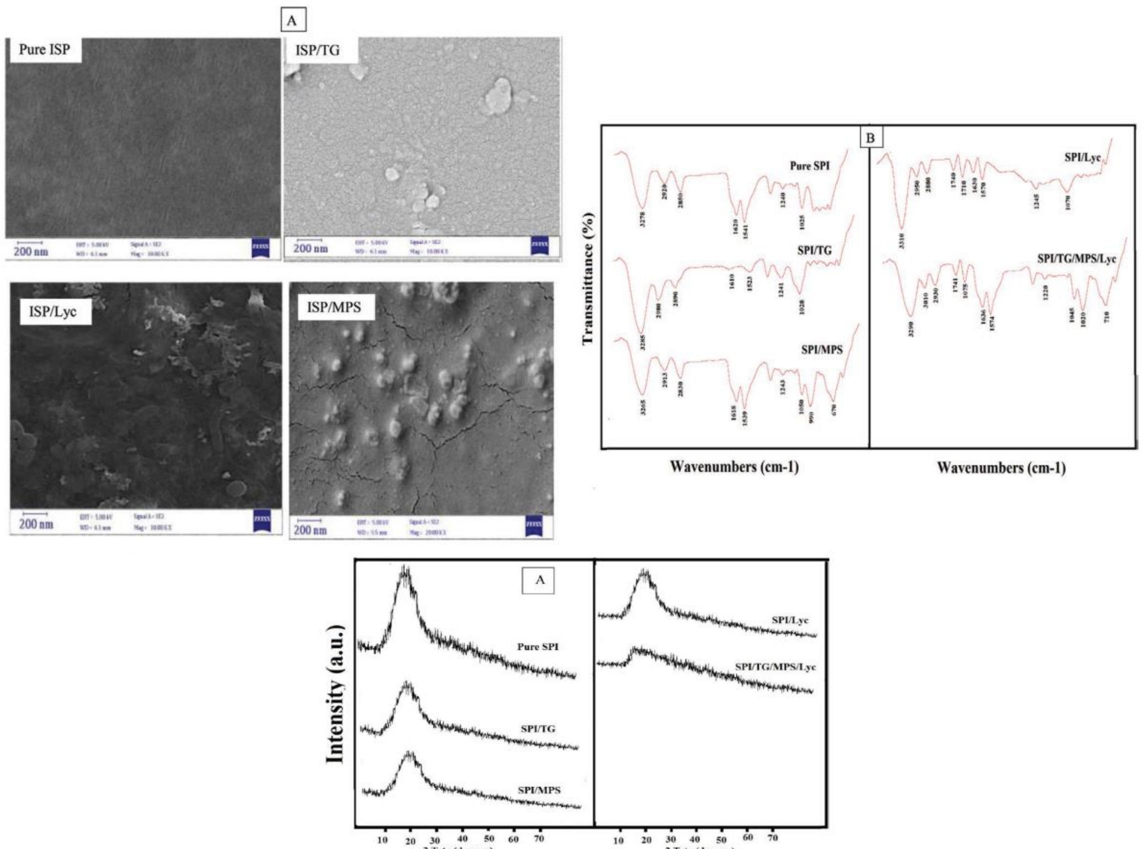

Figure 2. SEM images, FTIR spectra and XRD of ISP biohydrogels

Figure 2 also shows the spectra of XRD of ISP biohydrogel and its composites. According to the XRD spectra, as seen in the pure ISP spectrum, only a very wide peak in the 2θ of 15°–22° is seen, which indicates the amorphous structure of ISP. Previous research has shown that ISP is noncrystalline. The lowest height, is related to the ISP/TG/MPS/Lyc composite biohydrogel. Silica’s XRD peak also appears at ≈2θ of 20°, which overlaps with ISP peak.

3.3. Removal of Pollutants from Urmia Lake Sediments

with Biohydrogel To investigate the effect of ISP biohydrogel and its composites on the removal of Lake Urmia sediment pollutants, the sediment solution of this lake was treated for 1, 2, and 3 h with five optimal biohydrogel (according to Table 1B) and the removal efficiency of BOD, COD, nitrate, and nitrite were examined. Table 1 shows the removal efficiency of contaminants treated with different biohydrogels at different times.

Table 1. Removal efficiency (RE%) of contaminants treated with different biohydrogels at different times.

Biohydrogel type	Time (hour)	BOD	COD	Nitrite
ISP	1	25	35	31
	2	31	38	38
	3	39	43	43
ISP/TG	1	36	41	36
	2	42	45	45
	3	47	48	51
ISP/MPS	1	32	40	43
	2	35	44	48
	3	41	47	54
ISP/Lyc	1	24	34	75
	2	32	37	79
	3	38	42	82
ISP/TG/MPS/Lyc	1	41	47	81
	2	45	52	83
	3	49	57	87

Figure 3 also shows the column diagram of the efficiency of removal of BOD, COD, nitrate, and nitrite by five types of biohydrogel in three different treatment times. As can be seen from the results, all five biohydrogels have the ability to reduce BOD, COD, nitrate, and nitrite in sediments. As the treatment time of the biodegradable sedimentation solution increases, the efficiency of pollutant removal nincreases. The lowest removal efficiencies are related to purenISP biohydrogel. In ISP/TG biohydrogel, the removal of all contaminants has increased with the addition of tragacanth gum tomthe biohydrogel structure.

As the results showed, with the addition of tragacanth gum to the ISP structure, the humidity content and the WAC increased.nAs the biohydrogel WAC increase, the pollutants become more in contact with the biohydrogel polymer network, increasing the likelihood of physical contact and thus increasing the percentage of pollutant removal. The rate of elimination of pollutants in ISP/MPS biohydrogel also shows a relative increase compared to pure ISP. Due to the porous structure of silica nanoparticles, the placement of these particles in the isolated polymer chain of soy protein increases the internal porosity of biohydrogel, which leads to increase biohydrogel contact with pollutants and increases chemical interactions with biohydrogel, and therefore removal efficiency also increases.

In ISP/Lyc biohydrogel, the elimination of BOD and COD pollutants did not differ significantly from that of pure ISP biohydrogel, and the rate of nitrate removal increased slightly. But what is remarkable is that the rate of nitrite removal in ISP/Lyc biohydrogel has increased significantly compared to pure ISP biohydrogel. The significant increase in the nitrite removal efficiency indicates chemical interactions between lycopene pigment and nitrite. It is noteworthy that in the interaction of ISP/ Lyc biohydrogel with nitrite, the red color of the Biohydrogel goes to colorlessness, in other words, the higher the concentration of nitrite, the more colorless the red color of the biohydrogel. Also, nitrate has no effect on ISP/Lyc biohydrogel color.

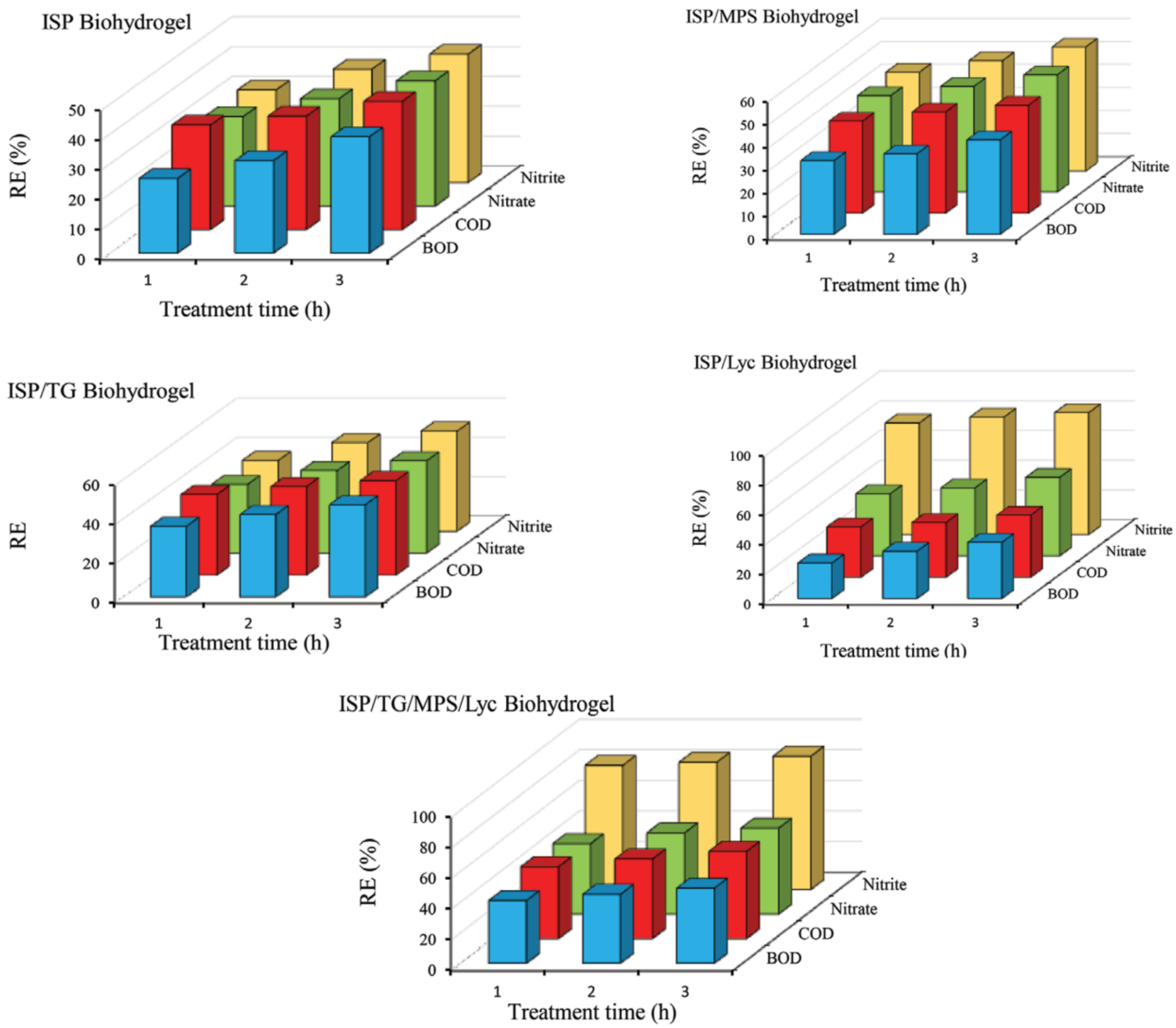

Figure 6. The effect of biohydrogel type and time on the removal efficiency of pollutants from lake sediments

4. Discussion

The possible mechanism for the interaction of lycopene with nitrite is as follows: Nitrite (NO_2^-) is converted to nitrosyl cation ($^+N{=}O$) in aquatic environments, where nitrosyl may be breaking the double bonds in the lycopene structure and destroying the lycopene structure (discoloration of the lycopene pigment confirms this) and nitrosyl itself is trapped in the structure of lycopene and loses its carcinogenic power, or in other words, is eliminated from the environment. As we know, nitrite converted to nitrosyl cation can react with dialkyl amine to produce carcinogenic nitrosamines. The fact that lycopene does not have a significant effect on nitrate removal may be due to the fact that nitrate cannot be converted to the nitrosyl cation ($^+N{=}O$) in aquatic environments and cannot break the double bonds in the lycopene structure, so the discoloration of the lycopene does not occur. In ISP/TG/MPS/Lyc biohydrogel, due to the fact that both tragacanth and porous silica nanoparticles and lycopene pigments are present and this biohydrogel has the highest moisture and the highest WAC, this biohydrogel has the most contact with pollutants and the most removal efficiency of BOD, COD, nitrate, and nitrite. However, in ISP/TG/MPS/Lyc biohydrogel the highest removal efficiency related to nitrite contaminant removal. In other words, the target of BOD, COD, and contaminants is probably only physical, while in addition to physical removal, chemical removal also occurs in nitrate removal. Khopde et al. examined the mechanism of reaction and trapping of NO_2 molecules in the polymer chain of carotenoids. The results of Khopde et al. confirm the results of the present study and the proposed mechanism [11]. Cerón-Carrasco et al. theoretically and using software calculations examined the interaction of NO2 and beta-carotene radicals, their results are in line with the results of the present study [12].

Conclusions

In this study, biohydrogel was prepared based on isolated soy protein/tragacanth gum/mesoporous silica nanoparticles/ lycopene. Biohydrogel properties showed that this biohydrogeln could absorb water 3–4 times its weight. Lycopene and silica nanoparticles reduced solubility. Tragacanth gum increases the moisture content and water absorption capacity of biohydrogel. Biohydrogel has a completely amorphous structure that its amorphous is increased by the addition of tragacanth gum, mesoporous silica nanoparticles, and lycopene. SEM images showed that tragacanth gum, mesoporous silica nanoparticles, and lycopene make cracks in the biohydrogel structure, and the distribution of silica nanoparticles on the biohydrogel structure was confirmed. According to the FTIR results, there is only physical interaction between lycopene and isolated soy protein, and electrostatic interactions were confirmed between isolated soy protein and tragacanth gum and silica nanoparticles. Five types of biohydrogel were used to treat Lake Urmia sediment solution. The results showed that all biohydrogels have the ability to reduce BOD, COD, nitrate, and nitrite, but biohydrogels containing lycopene pigments remove much more nitrite contaminants than other contaminants. In other words, the biohydrogel containing lycopene selectively purifies nitrite from the sediment solution of Lake Urmia.

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