RESEARCH ARTICLE

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Studying the Adsorption Behavior of Copper Ions in Industrial Wastewater, Using Modified Electrospun Polymeric Nano Fiber

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Background & Aims of the Study: Soil and water pollution to heavy metals is a serious threat for environment and human health. Finding an effective way for refining water from these metals is very important. The aim of this study was modifying electrospun polymeric nano fibers and studying its efficiency for copper ion omission in water solutions.

Materials & Methods: In this study, nano fiber was produced by solution electrospun polystyrene in DMF/THF solvent and produced nano fiber was used for copper pre-concentration in waste water sample. In this study, an investigation of primary PH of solution, adsorption particle size, cleaning solvent volume, salt supply, contact time duration of adsorption material on copper ion adsorption supply was done, using modified nano fiber.

Results: According to this study, copper adsorption process with correlation coefficient of (R^2) in scope of 0.986 by Langmuir and Freundlich are describable. Findings show that, pH optimized amount for isolating copper ion on absorbent level is 7, absorbent particle size is 0.006 g/l, salt 1.3, potassium nitrate and the contact time of absorbent material on copper ion adsorption is 10 minutes. Copper ion adsorbate was cleaned, using 0.7 ml methanol. Most of obtrusive ions didn't have any inconvenience for copper ion isolation and measuring. The mean of the method was 2.7 µg/l and standard deviation was lower than 4%.

Conclusions: this method was done on actual samples which findings show that, this method has the ability of cooper adsorption and can use this method for measuring heavy metals like copper in different tissues. This method because of having the privilege for isolating and pre concentrating different kind of mineral and organic is used successfully in different samples.

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Background

Today water source pollution is one of the serious problems. Among different kinds of contamination, we can mention heavy metals, radioactive compounds, organic and nano organic compounds. Heavy metals have a significant importance in environment pollution because they can't be analyzed, and have

harmful physiological effects on living creatures (1) Copper (II) is one of the important elements for plants and animals; But large amount of it is toxic for all living creatures. Most hazardous human activities like mining, metal melting, domestic and industrial sewage ooze applications in agricultural lands, using copper as a fungicide pesticide cause soil and water pollution to copper. High levels of this metal effect on ecosystem microbial population. Removal of heavy metal ions from water and industrial sewage is very important and has drawn attention of most of researchers (2-4). Nowadays, because of industries improvement and entering waste water of industrial factories to ecosystem, environment and underground water, the pollution risk is developed which has harmful effects on living creatures, soil, also plants and animals of these regions in long and short terms (5-7). Heavy metals are the most common contaminations that are found in high concentration and cause irreparable harms to ecology. Mechanism of toxic effects of heavy metals like copper from bio chemistry prospective is strong tendency of cations of these metals to reaction with sulfur (8-10). Heavy metals which are copper, chrome, cadmium, nickel and zinc have tendency to be gathered in food chain (11-12). Cations of these metals or those molecules which have these metals enter into the body by ingestion and they will attach to Solfhydryl groups which there are plenty of them in body (13). Sulfuric bonds joint effects on those enzymes which control metabolism reaction speed in body; so, these enzymes can't do their normal works and put human health in risk of illnesses that sometimes it is fatal (14-15). Illnesses which are caused by heavy metals like copper are dermatitis, Asthma, Bronchitis and in some sources it is mentioned copper cause cancer. Spreading heavy metals to the environment is happened by different processes and ways such as air, surface water, soil, underground water and plants. When copper is absorbed by mud, it can go a long way and contaminates the surface water and soil. Different ways are used for omission of heavy metal ions from water solution which are ion alternation, reverse osmosis, electro chemical sediment, ion replacement, membranes processes, evaporation and absorption for ion omission of heavy metals from water solution (16-18). Among mentioned methods in recent years, absorption method is important because it is a simple, cheap and an effective way for heavy metals ion omission. Nano fiber is used in this study because of high absorption efficiency, special level and active places. In this research, analytical method for solid phase was used for separating copper cation and measuring was done by flame atomic absorption which has effective factors for efficiency extraction such as pH effect, adsorption supply, cleaning solution type and concentration. Samples' size were checked and optimized by flame atomic absorption spectrometry. Interference effects of other ions and analysis parameters, kinetic and thermodynamic were computed. This method was used effectively for actual samples such as natural water (19).

Aims of the study:

The aim of this research is using electrospun polymer nano fiber coated with ligand for copper ion omission from water solution and industrial wastewater.

Materials & Methods

In this study which is an experimental one, absorption rate from industrial waste water was investigated, using polymeric nano fiber absorbent. For preparing mother solution, 1000ppm copper cation from salt $Cu(NO_3)_2.3H_2O$ was used and other necessary. Solution was produced by repeated dilution of primary solution with deionized distilled water. Also, solution of 1000 mgL^{-1} used ions in harassment investigation phase were prepared by solving sufficient copper salt in deionized distilled water. Acetate buffer was prepared by Neutralization of hydrogen chloride by sodium hydroxide to reach pH=7. Polystyrene and

dithizone complexing agent was prepared by references. Other used solution like Aceton, Tetrahydrofuran, Dimethylformamide, and acids such as nitric acid, acetic acid, sulfuric acid, phosphoric acid which had sufficient analytical purity and all of the mentioned materials were bought in Merck Co. Equipment's which were used in this study were optical microscope, SEM, Electrospinning, device made in Iran for polystyrene fiber production, Flame atomic absorption spectrometer made by Shimadzu, AA-680 model. For measuring copper cation concentration which were used in parameter optimization stage, peristaltic pumps LAMBDACZs.r.o was used for sample solution passing from column containing the adsorbent. For measuring solution pH, pH meter device Lab -827, equipped with compound glass electrode, was used. Ultra sonic bath VGT-173OQTD was used for homogenization.

For preparing absorbent, first pour 500mg polystyrene in a test tube and add Dimethyl formamide and Tetrahydrofuran compound to Polystyrene completely dissolve. Finally, it had obtained viscose solution (20). The final solution was kept in 25c' temperature for three hours. Then, for more homogenization, the final solution was put in Ultrasonic bath for 15 min in 20 degrees Celsius. Then, 30 mg Dithizone was added to the produced solution for complete reaction between polymer and ligand modifier was put in Ultrasonic bath in 20c' for 30 min. We inject the final solution to electrospun machine and nano fiber was obtained in an optimal condition. Obtained nano fiber diameter was investigated by light and electron microscope, see findings in figure1. Polystyrene formation mechanism is shown in figure 2.

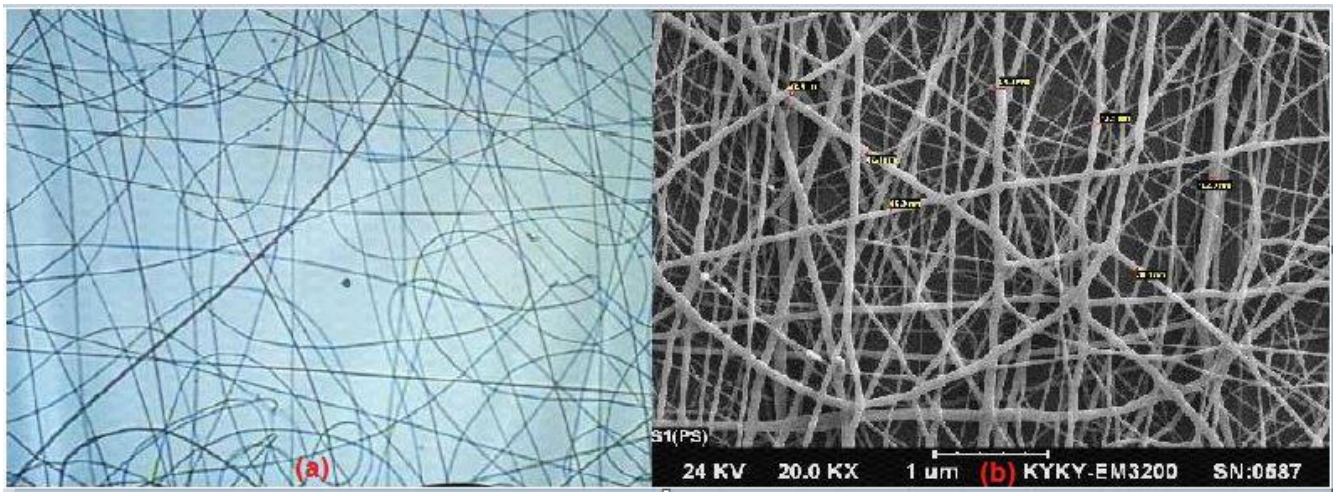

Figure 1) Electron microscope picture of produced nano fiber (a) light microscope picture of nano fiber (b).

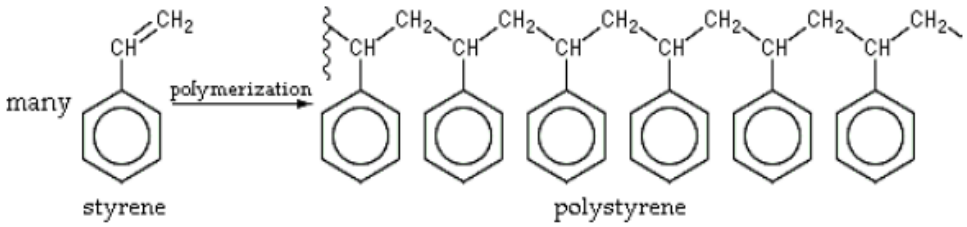

Figure2) The mechanism of polystyrene formation.

In order to optimization of effective factors on absorption before doing this absorbent process, first should recognize effective factors on absorbent then optimize them. For this purpose, pH amount effect, absorbent supply, salt concentration effect, contact time effect was determined for each test. Thus, determined amount of produced nano fiber was put into a micro tube by 5 ml ethanol and deionized distilled water was passed for absorbent compression. Then, prepared solution contains copper with o.2 mg ml-1 concentration passed through pump after that cleaning was done completely. Taken sample was investigated by Flame atomic Absorption spectrophotometer. Four effective parameters for copper absorption were investigated. In way which in each test, three parameters are fixed and one parameter is variable. Thus, it can investigate the effect of variable parameter on copper cation absorption.

Results

pH effect

One important parameter in absorption is primary solution pH. The results of pH effect on copper ion absorption are shown in figure 3. By increasing solution pH from 3 to 7, mentioned ion omission increase. So, PH=3 has the lowest absorption and pH=7 has the highest absorption. According to findings, we could mention that, by increasing pH to optimum amount, absorption amount increase. The reason can be explained that, in pHs lower than optimized pH because of ligand protonation and complex tendency deduction with ion, ion absorption and recovery rate decrease. In pHs upper than optimized PH, the percent of recovery decrease because of metal hydroxides formation.

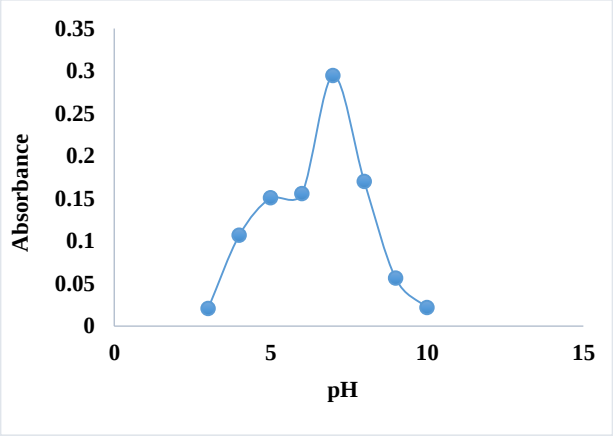

Figure3) pH effect on copper absorption

Effect of modified nano fiber

Solid phase column filler is an important parameter and its optimization is necessary. The effect of modified nano fiber absorbent on copper ion absorption was investigated. By increasing absorbent rate, available absorption places for copper increase and absorption was done better. To determine the effect of absorbent rate on copper omission, absorbent rate was determined in 0.002 to 0.01. According to figure 4, by increasing the absorbent rate to optimized level, the absorption rate increase that results confirm that by increasing absorbent rate to optimized level because abound of rate level, the number of active places for complexion of copper ion increase; thus, increase the absorption process, when absorbents rate reach to it's maximum performance of 0.006 gr/l, the number of active places and absorbent surface are responsive for copper ion numbers in solution in equilibrium adsorption process. Increasing the absorbent rate to optimized level cause the contact time increase which increase ion absorption percent.

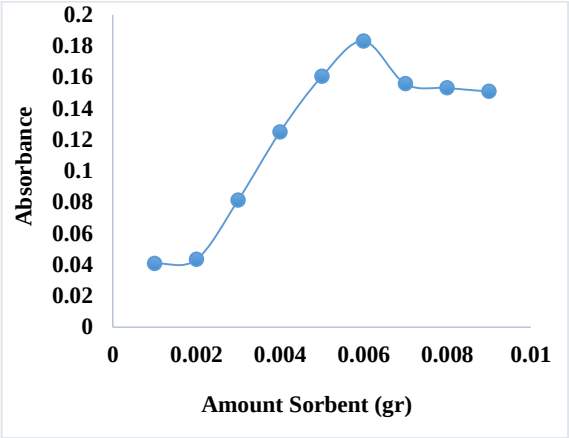

Figure 4) absorbent effect on absorption rate

Investigation of salt concentration:

Salt increase has different effects on adsorption efficiency. Maybe, improved adsorption, decrease it or be effect less (20,21). Figure 5 shows the decomposition response changes according to concentration response of potassium nitrate in 0.1 to 2 gr range of this salt. As it can be seen in figure 5, increasing salt concentration to 1.3 gr, increase efficiency extraction, after that extraction decrease. Maybe decomposition response deducted because of that, after a determined concentration of salt, physical properties of extraction layer will change and analyte adsorption rate decrease.

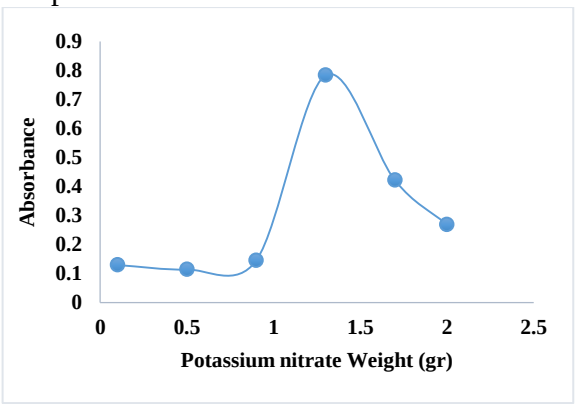

Figure 5) Salt concentration effect on absorption rate.

Investigation of contact time effect

The investigation of the contact time is shown in figure 6 that copper ion absorption by modified absorbent has higher velocity, so, 16 percent absorption in 1 min and 62 percent in 60min was seen. According to findings, absorption velocity in first 10 min is higher than other times and after 60 min, desorption take place. It could be related to high sample surface area and abound of active agent groups for copper ion complexion. Absorbent selectivity for heavy metal absorption is related to metal properties. Some properties such as metal ionic radium, atomic weight, electronegativity, fixed hydrolysis and softness are effective on up take efficiency and when they increase, up take efficiency rate increase.

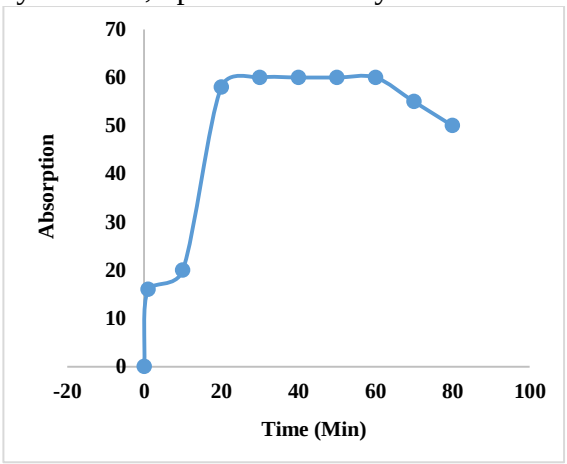

Figure 6) contact time effect on absorption rate

The type and volume of solvent

Absorbing solvent should be able to absorb analytes from absorption level. It doesn't have damaging effects on species structures. By suitable cleaning of inhibited analytes from column, we can determine repeatability and accuracy of the method. To select the best of washer, 5mL analyte solution, 10ppm copper concentration, 0.006 absorbent rate in pH=7 was passed in column, then absorbed ion cleaning was investigated by 0.5 mL ethanol, methanol and Acetonitrile. According to figure7, findings showed, by methanol as a cleaning solvent, we will reach to the highest rate of absorption. So, methanol solution has higher ability to clean analyte. Recovery level deduction of copper ion with other cleaning solution can contribute to deposit copper ions

with existing anionic foundation in structure of these solutions.

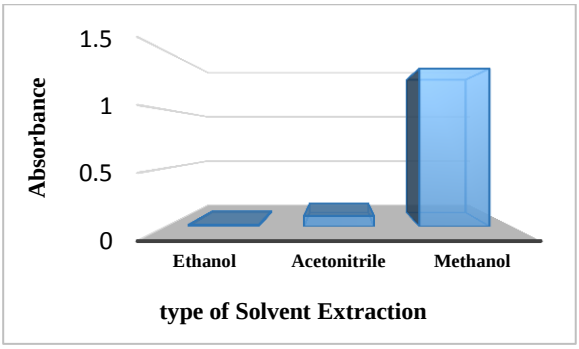

Figure 7) copper ion adsorption changes, based on solvent volume variations

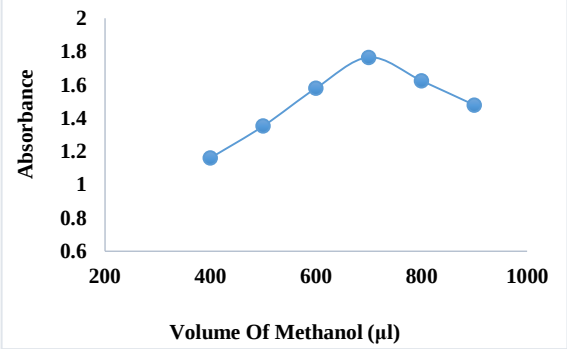

Figure 8) Copper ions adsorption changes based on solvent type variation

Determine method detection limit

The lowest concentration from sample that the answer of machine is meaningfully different from control signal is the limit of detection. For determining the detection limit (DL), control solution the adsorbent under optimized condition and suggested. Solution was investigated by Atomic absorption spectrometry; so, the limit of detection was 2.70 mg/l.

Investigation of repeatability and accuracy of method

Accuracy shows the repeatability rate of method which is shown by relative standard deviation or RSP which is a function of sample concentration. For studying repeatability of method, 8 solutions of 50 ml with 0.2 μgmL^{-1} concentration from copper cation were recycled, using solid phase extraction method. Standard deviation was 1.7.

Measurement of copper cation in real samples

For measuring the ability of suggested method to assess heavy metals in water samples with different tissues, this method was used for isolating and measuring of copper ions from different water under optimized condition. To investigate the accuracy of method and it's suitability, standard additional method was used. The extraction and recovery of cation cu^{2+} take place. The result of method accuracy in real sample is seen in table1. As the results showed, samples tissue has a meaningful effect copper cation extraction and the suggested method has a good performance for copper cation extraction from different tissues.

Table 1) copper absorption in real samples

Piped water	Cu^{2+} (μgL^{-1})	Absorption	Recovered (%)	RSD
Arak	0	Not seen	---	**---**
	100	97.14±0.01	97.14	**0.60**
	200	198.3±0.01	99.15	**0.80**
Ashtian	0	Not seen	---	**---**
	100	95.16±0.03	95.16	**1.70**
	200	194.27±0.04	97.13	**2.20**
Farmahin	0	Not seen	---	**---**
	100	96.8±0.2	96.80	**0.99**
	200	95.16±0.02	96.40	**0.39**

Absorption isotherm

Freundlich and Langmuir absorption isotherm are shown in figure 8. The diagram of C_e/q_e against C_e showed langmuir isotherm and diagram of log q_e) against log C_e showed Freundlich isotherm. There are different parameters in figure 9. Numbers which are higher than R^2 in this relation showed that experimental data follow freundlich and langmuir relation. The result of isotherm studies showed that, fixed N for freundlich studies is bigger than 1 which shows the sufficient condition for copper absorption process with modified electrospun polymer nano fiber.

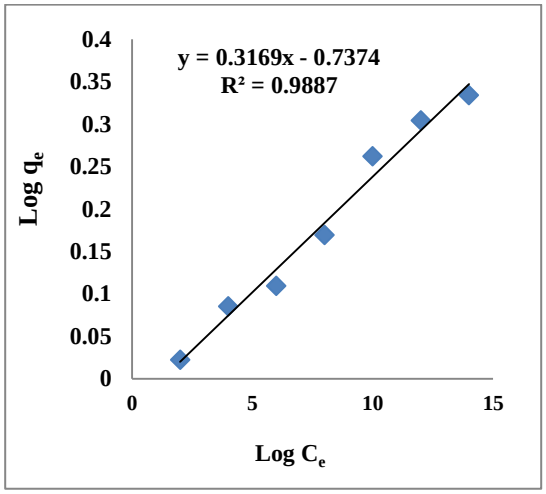

Figure 9) copper absorption isotherm by modified electrospun nano fiber with ligand

Absorption kinetics

Absorption is a multi-step process which include transfer of adsorb molecule from solution phase to absorbent surface then entering of solute particles to internal pores. For kinetics studies, obtained absorption amount on 500mgr modified nano fiber with ligand in 2 μgmL^{-1} concentration is volume of 100ml from ion cu^{2+} was studied in different times near the absorbent in optimized condition. Kinetics models were used on experimental data to investigate the absorption process and potential of rate determining step. According to coefficient correlation, we can predict compliance of absorption process from each equation. According to obtained information, we can conclude that, absorption on modified electrospun polymer nano fiber of second grade kinetics as speed controller steps and comply with descriptor of mass transfer mechanism.

Discussion

There has been various methods for omitting heavy metals out of industrial waste waters so far,for instance omitting copper out of watery solutions by biological methods, that hasn't had important effects on omitting this kid of metals (22) while This study has shown that, in optimized condition (pH, absorbent supply, contact time, kind and volume of cleaning solution, salt concentration), the maximum of copper adsorption by modified nano fibers, using dithizon modifier was 94 percent. The results showed, pH had an important role. Copper omission efficiency decrease by increasing or decreasing of pH, because in pHs lower than an optimal pH due to ligand protonation and decreasing tendency to ion complexion adsorption, it's salvage will decrease. In a pH which was upper than optimized pH, because of metal hydroxides, the salvage percent decrease (23). Investigation of adsorption rate showed, by increasing the adsorbent rate, copper omission increase and maximum of copper adsorption in absorbent concentration was 0.006 gr/l, so, by increasing the absorbent supply, more than 0.006 gr/l omission random was not significant and adsorption rate decrease; because the number of active places on absorbent level were sufficient for metal ions in solution in balance adsorption process. Actually, increasing the absorbent rate to an optimum supply cause increasing the contact level which increase ion adsorption percent. Results showed, by increasing the salt concentration level from 0.001 to 1.3 and from 1.3 to 2 gr, decrease copper adsorption rate. We can say, it happens because of some limitations in adsorption place, its saturation level and physical specification changes of adsorption

level. The results of experiments on effects of contact time changes on copper adsorption level showed, by increasing the contact time, because of increasing velocity and chance of copper ions, encountering with adsorption particle increase; but when contact time between absorbent and ion solution increase, metal ion attraction by absorbent will increase. Also, there is a relationship between ion deduction and it's steadiness with absorbent adsorption valence. There will be a balance between solid and liquid phase, and by increasing more contact time, adsorption and phenomenon take place. This study shows modified nano fiber is an effective absorbent in copper absorption of water solutions. Solution pH has an important role in adsorption process. pH neutral in a way that increases the absorption rate. By computing isotherm constants, Freundlich and Langmuir adsorption were similar, and follow isotherm condition and hypothesis. According to the results of adsorption experiments, kinetic is more similar to second grade model.

Conclusion

Conclusions

Nowadays, the danger of waste water contain heavy metals is the most important environmental problem in the world. There are different ways in this field but there are some problems with them such as destroying environment or expensive absorbent. In this study, copper omission from industrial waste water by modified poly styrene nano fiber with dithizone which is prepared by electrospining was investigated. First, effective agents on process were investigated. Results showed, an optimal condition for copper omission was absorbent rate 0.006, pH=7, solvent detergent of ethanol solution=0.7ml and salt=1.3gr. This method was done on real samples which show this method can omit heavy metals specially copper. This method can be used for measuring heavy metals in different tissues. This method has some privilege; it needs less chemicals specially harmful organic solvent, high repeatability, low cost, their coupling ability with different instrumental techniques, high selectivity for isolation and preconcentration of different organic and mineral species in different samples are used successfully. Finally, it is suggested to use this method in Iran waste water industry.

Footnotes

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Conflict of Interest:

The authors declare no conflict of interest.

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