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Research article

Simulation of chromium, nickel and lead removal from aqueous environment using polypyrrol and its composites

Arash Shabani[1], Majid Riahi Samani[1*], Davood Toghraie[2]

[1]*Department of Civil Engineering, Khomeinishahr Branch, Islamic Azad University, Khomeinishahr, Isfahan,Iran*
[2]*Department of Mechanical Engineering, Khomeinishahr Branch, Islamic Azad University, Khomeinishahr, Isfahan, Iran*

*riahysamani@iaukhsh.ac.ir

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Abstract

The unique chemical and physical properties of heavy metals have led to their use in various applications in manufacturing industries. The metal used in these industries is usually directed to the waste water and can cause environmental problems. In the present study, removal of chromium, lead and nickel by using polypyrrol and its composites from the aqueous environment were simulated. Batch quarantine method was used to measure the removal of these metals from the aqueous environment. The simulated results showed that all polypyrrols and their composites are suitable for the removal of +6 chromium. The highest adsorption of total chromium and +6 chromium was observed by polypyrrol and polyethylene glycol composites with 90.7% and 96.2%, respectively. However, polypyrrol and its composites are undesirable for removal of lead, cadmium and nickel. The highest removal rates of lead and cadmium by activated carbon powder were 99.5% and 78.08%, respectively. Also, the percentage of nickel removal by some polypyrrols was lower than activated carbon with 14.96% removal. Some polypyrrols also have a higher percentage of knockout than activated carbon, which does not seem very high in comparison with other heavy metals. In general, it can be found that the use of polypyrrol composites, especially polypyrrol and polyethylene glycol composites, are suitable for the removal of total chromium and +6 chromium from the aqueous environment, but are undesirable for the removal of lead and nickel.

Keywords: Heavy metals, Removal simulation, Polypyrrol, Composite, Aqueous environment.

1- Introduction

Water is an essential substance for life on Earth and a part of the body of all living things. Plants and animals need almost pure water for their lives [1]. Unfortunately, in addition to the gradual reduction of existing water reserves, various types of pollutants have caused many problems [2]. In recent years, with the continuous development of industry and the global economy, large quantities of industrial wastewater containing heavy metals have been released directly into natural waters without any treatment, so that the number of heavy metals in aquatic environments has increased greatly [3-4]. Water pollution is considered a major challenge in the world. Both surface and groundwater are exposed to various pollutants [5]. According to WHO reports, UNICEF approximately 70-80% of all diseases in developing countries are caused by various water pollutions [6]. Heavy metals are the main environmental pollutants due to their high toxicity and pose a serious threat to humans and organisms in high concentrations [7]. If the density of each metal in water is greater than 5-3 g/m, it is considered as heavy metal, various industries such as mining, leather industry, textiles, paper factories, etc. Each produces different heavy metals that may enter the aquatic environment [8]. These metals reach the water of ponds, rivers, lakes, seas and oceans and pose a serious threat to all environmental residents. Metals released into the aquatic environment accumulate indefinitely in the living tissues of organisms along the food chain [13-14]. Heavy metals that can cause kidney damage, anemia, hemolysis, liver dysfunction and nerve cell damage [15]. The removal of toxic heavy metals such as chromium, copper, lead, nickel and cadmium from the aquatic environment has attracted much attention in recent years due to its toxicity and carcinogenic properties that may damage various systems of the human body [16-18].

Currently, various methods are used to remove heavy metals from aquatic environments, such as chemical deposition, reverse osmosis and adsorption, each of which has its advantages and disadvantages. Chemical deposition produces a large amount of sludge, which is very difficult to manage and dispose of the produced sludge. Reverse osmosis method produces wastewater and consumes a lot of energy and electricity. Today, scientists are looking for a new adsorbent to remove heavy metals from the aquatic environment [19-20]. Adsorption is a method based on chemical or physical interactions between pollutants and adsorbents that lead to pollutant absorption, this method is used in wastewater treatment which leads to the removal of heavy metals through an inexpensive and simple technology [21]. The use of polymers such as polypyrrol as a new generation of environmental pollutants adsorbents leading to the removal of heavy metals from the environment has been considered in recent decades [22].

Since the emergence of Polymers, the use of these materials as insulators has been thought in the mind, but in recent years a new group of polymers have been synthesized which are electrical current conductors and are called conductive polymers. All conductive polymers have double bonding [23]. polypyrrol is one of the conductive polymers that usually has high conductivity and special capacity and easy preparation. Conductive polymers have shown high potential for ion removal from water due to the ion exchange properties between polymer and environment. Ionic exchange of conductive polymers is a 3D process [24]. Polypyrrol has characteristics such as lack of toxicity, environmental stability, inexpensiveness, easy center and exchange of ion properties in order to absorb heavy metals [25]. Polymer chains in this polymer have positive charges that are surrounded by anions (usually nitrate, chloride, perchlorate and sulfate), so the positive charge of the polypyrrol spine has made it into a polymer with potential ion exchange [26-27]. Nitrogen atoms with positive charge in polypyrrol may be very inclined to bind with heavy metals [28]. Composites refer to a group that uses the physical composition of two or more ingredients at the macro level to create a new material with superior physical and mechanical properties than ingredients that retain their characteristics and do not dissolve or mix in each other [29].

In this regard, Birniva et al. (2021) investigated polypyrrol-polyethylene nanocomposite (PPy-PEI): an effective adsorbent for nickel ion absorption from aqueous solution. The obtains showed that polypyrrol- polyethylene (PPy-PEI) nanocomposite in an optimum equilibrium system had an adsorption rate of 0.08 g nickel ion at 4.5 pH and 60 min contact time at room temperature [30]. In this study Rafi et al. (2020) removal of hexavalent chromium from the aquatic environment using pomegranate skin modified with polymer coatings: The effects of different composite composition components were investigated. In this study, pomegranate peel powder (PGP) modified with polyaniline (PANI) and polypyrrol (PPy) was used to remove Cr (VI) from the aqueous environment. The effects of different parameters of composite synthesis including solvents and stabilizers such as polyvinyl alcohol (PVA) and polyethylene glycol (PEG) concentrations were investigated under different conditions and the most suitable composite capable of removing the highest percentage of chromium was determined. The excretion results showed that the PGP-PPy composite synthesized in water/butanol was able to excrete 93.75 chromium from the aqueous environment [31]. Research by Zang et al. (2019) on the elimination of heavy metal ions using polypyrrol/chitosan composite electrodes showed that the net absorption capacity of this composite was good for heavy metals such as lead and cadmium and this material has the ability to remove heavy metals from contaminated water [32]. The unique chemical and physical properties of heavy metals have led to their use in various applications in manufacturing industries. The metal used in these industries is usually directed to the waste water and can cause environmental problems. In the present study, the removal of heavy metals chromium, nickel and lead from aqueous environment using different polypyrrol composites has been simulated.

2- Materials and Methods

2-1- Materials used in the testing

Pyrrole (99%) of Merck Company was used as a monomer. Polyvinyl alcohol (PVA) 72000=MW, polyethylene glycol (PEG) 35000 MW, ferric chloride, sulfuric acid, chloride acid, acetone, acetonitrile, ethyl acetate, and activated carbon pour were all prepared in laboratory and from Merck Company. Lead nitrate, nickel nitrate and potassium dichromate have all been purchased from Merck Company and have been used for preparation of standard solutions such as chromium, lead and nickel according to molar mass and purity percentage. Distilled water without ion was used in all stages of the experiment.

2-2- Equipment used in testing

The equipment used in this study included pH meter model P-M-T-Model 2002 manufactured by HANNA Company, magnetic stirrer model MR 3001 K, filter, degradable scale model EP 211 D, Varian atomic absorption device model Spectra AA, Spectrophotometer from Varian 300 company.

2-3- Synthesis method of polypyrrol composites

2-3-1- Preparation of poly-pyrrol in aquatic, non-aquatic environment

In order to prepare polypyrrol in aqueous and non-aquatic environments, 100 cc of water without ion and 100 cc of other solvents including ethyl acetate, acetonitrile each with 8 g iron (100 cc) III) chloride, which has been used as oxide, mixed using magnetic stirrer and then filtered by filter to remove its impurity and obtain a uniform solution. Then 1 cc newly distilled old monomer was injected into it and the resulting solution was placed on the magnetic stirrer for 5 hours and mixing was performed. By injecting the old monomer, the solution changes color, first the orange is dyed and then black, indicating the conversion of monomer to polymer. After 5 hours of stirring by the magnetic stirrer, the solution was smoothed and to eliminate the existing oligomers and impurities, the resulting polymer was washed several times with distilled water without ion. The obtained polymer was dried to prepare the powder at the ambient temperature. Similar to the process of polypyrrol center for preparation of other derivatives, the same process was repeated.

2-3-2- Preparation of polypyrrol in aquatic, non-aquatic medium with polyethylene glycol and polyvinyl alcohol

For this purpose, 100 cc of water without ion for preparation of polypyrrol and polyethylene glycol in an aqueous environment and 100 cc of different solvents, including ethyl acetate and acetonitrile for its preparation in non-aqueous environment, each with Mix 8 g of iron III hydrated chloride used as oxidant and smooth using magnetic stirrer and then filter until impurity is taken and a uniform solution is obtained. Then, add 0.2 g of polyethylene glycol powder to it, put the resulting solution on the magnetic stirrer for 30 minutes to obtain a uniform solution. Then, 1 cc of newly distilled old monomer was injected into it and the resulting solution was placed on the magnetic stirrer for 5 hours and mixing was performed. By injecting the old monomer, the solution changes color and the resulting orange solution is blackened after a while, which indicates the conversion of monomer to polymer. After 5 hours, the solution was stirred by magnetic stirrer, the solution was smoothed. To eliminate the existing oligomers and impurities, the resulting polymer was washed several times with ion-free water. The obtained polymer was dried to prepare the powder at the ambient temperature. In order to study polyethylene glycol concentration, the same experiment was repeated for concentrations of 0.4-6.4 g of polyethylene glycol.

2-4- Chromium, lead and nickel metals removal simulation

For this purpose, the specific amount of adsorbent was added to the specific volume of the solution containing heavy metal with specified concentration and pH and stirred by the magnetic stirrer for a certain period. Then, by passing the solution containing adsorbent from the filter paper, the adsorbent was separated from the solution and the initial and final concentration of heavy metal before and after separation was calculated using atomic absorption device and the percentage of heavy metal removal from relation and Eq. (1) was simulated.

$$R=100*(C_0-C_t)/C_0 \quad (1)$$

In this regard, C_0 is the initial concentration of heavy metal and C_t is the final concentration of heavy metal in solution.

3- Results and Discussion

3-1- chromium +6 removal simulation by using polypyrrol and its composites

According to Table 1 all Polypyrroles had a good performance in chromium removal and the percentage of chromium removal by all polypyrroles was higher than activated carbon with 23.6% removal. Among polypyrrol and its composites, polypyrrol synthesized in water solvent and ferric chloride oxidant in the presence of polyethylene glycol as additive with concentration of 32 g/L with 90.7% removal had the highest percentage of chromium removal (approximately 4.5 times more than activated carbon). And the lowest removal rate of chromium among polypyrroles and its composites was 39.93% according to the polypyrrol composite synthesized in now water /ethyl acetate. Among polypyrroles, those synthesized in water solvent / acetonitrile with a volume ratio of 50.50 and ferric chloride oxidant have the best performance in chromium removal.

Table 1: Effect of polypyrrol synthesis conditions on chromium removal simulation

Polymer type	Solvent	Additive material	Concentration of additives (gr/L)	Initial concentration of chromium (ppm)	Final concentration of chromium (ppm)	Percentage of Chrome Removal (%)
polypyrrol	water	-	-	50	22.82	54.4
polypyrrol	Acetonitrile	-	-	50	10.88	78.2
polypyrrol	Ethyl acetate	-	-	50	7.06	85.9
polypyrrol	Water+ Acetonitrile	-	-	50	6.34	87.3
polypyrrol	Water+ Ethyl acetate	-	-	50	9.08	81.8
polypyrrol	water	PVA	1.5	50	13.37	73.3
polypyrrol	Acetonitrile	PVA	1.5	50	7.46	85.1
polypyrrol	Ethyl acetate	PVA	1.5	50	10.54	78.9
polypyrrol	Water+ Acetonitrile	PVA	1.5	50	28.36	43.3
polypyrrol	Water +Ethyl acetate	PVA	1.5	50	30.03	39.93
polypyrrol	water	PEG	2	50	12.02	75.97
polypyrrol	water	PEG	4	50	10.78	78.44
polypyrrol	water	PEG	8	50	9.59	80.81
polypyrrol	water	PEG	16	50	8.71	82.57
polypyrrol	water	PEG	32	50	4.97	90.07
polypyrrol	water	PEG	64	50	7.04	85.92
Activated Carbon Powder				**50**	**38.18**	**23.6**

The results of chromium removal by polypyrrol synthesized in different solvents showed that the highest amount of chromium removal was in the polypyrrol group synthesized in water and ethylene acetate and the highest percentage of chromium removal was by polypyrrol composite and polyvinyl alcohol in polypyrrol and polyvinyl alcohol composites in acetonitrile solvent. Polyvinyl alcohol as an additive and surfactant with a concentration of 1.5 g/L on the efficiency of polypyrroles synthesized in water solvent and acetonitrile solvent alone, could increase the absorption of chromium, but the use of this material in ethyl acetate solvent and water mixture + acetonitrile and water mixture + ethyl acetate has been photographed and the efficiency of chromium removal has been reduced. Also, polyethylene glycol as an additive has been able to positively affect the removal efficiency of chromium by polypyrrol and increase the removal capacity of chromium by polypyrrol. The optimum concentration of polyethylene glycol was 32 g/L. Polyethylene glycol is a surfactant material and during the polymerization process, with the help of hydrogen bonds, the absorption of polymer particles is growing and affects the shape, morphology, uniformity, lateral surface, size and some properties of polypyrrole. SEM photographs taken from the surface of polypyrrol polymers and different concentrations of polyethylene glycol can be seen in Fig. 1, confirming this.

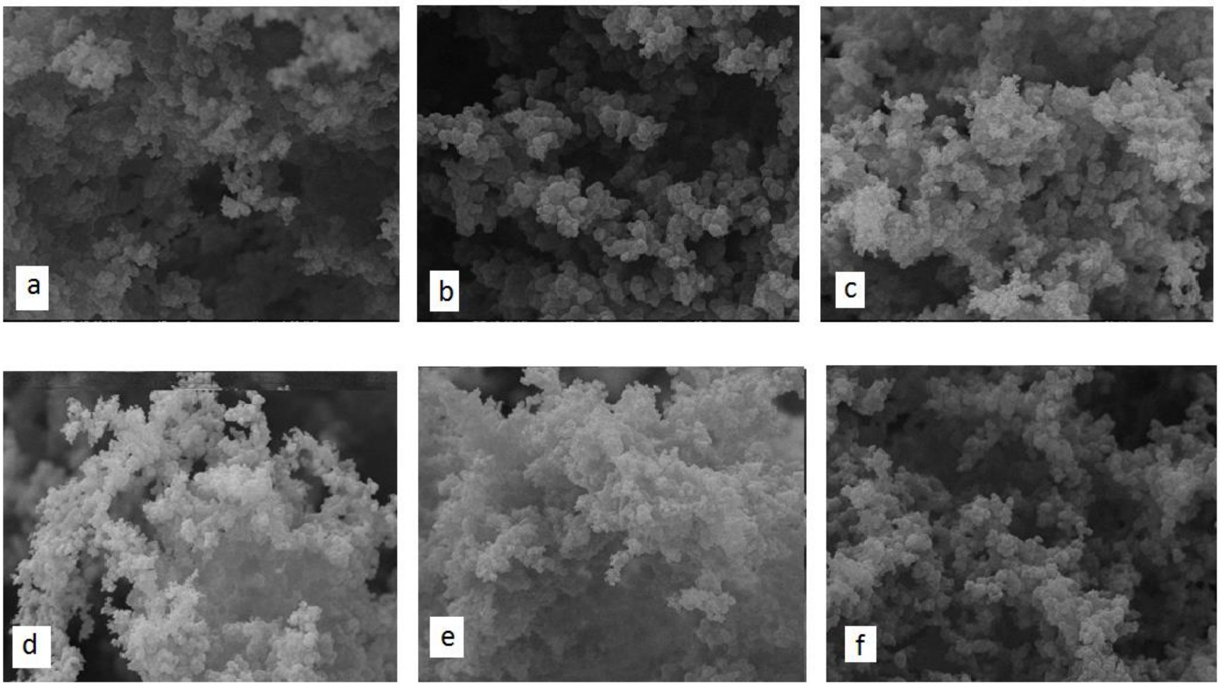

Fig. 1 SEM a)Polypyrrol-b composite polypyrrol and polyethylene glycol (concentration of polyethylene glycol 2 glycol/l)-c) Polypyrrol composite and polyethylene glycol (concentration of polyethylene glycol 4 glycol/l) (-d) Polypyrrol composite and polyethylene glycol (polyethylene glycol concentration 8 g/l) -e) polypyrrol composite and polyethylene glycol (polyethylene glycol concentration 16 g/l) -f) polypyrrol composite and Polyethylene glycol (concentration of polyethylene glycol 32 g/L) synthesized in water with a magnification of 4000x

3-2- lead removal simulation by using polypyrrol and its composites

According to Table 2, all polypyrroles have undesirable performance in lead removal and the percentage of lead removal by all polypyrroles is less than activated carbon with 99.5% removal. Among polypyrrol and its composites, polypyrrol synthesized in water solvent and ferric chloride oxidant in the presence of polyvinyl alcohol as additive with concentration of 1.5 g/L with 62.6% removal had the highest percentage of lead removal. The lowest removal rate of lead was 8.31% using polypyrrol and its composites in polypyrrol and polyvinyl alcohol composites synthesized in ethyl acetate solvent.

Polyvinyl alcohol as an additive and surfactant has a tremendous effect on the performance efficiency of polypyrroles synthesized in water solvent and has greatly increased their capacity to absorb lead. In acetonitrile solvent and water mixture + acetonitrile also polyvinyl alcohol has a positive effect but its effect is not dramatic. In other solvents, the use of polyvinyl alcohol has had a negative effect. Based on the results, polypyrrol and its composites did not show a suitable performance for removal of lead from aquatic environment compared to activated carbon powder, however, the use of polyethylene glycol in different concentrations could have a positive effect on lead removal from aquatic environment by polypyrrol composite and at 32 g/L concentration 34.75% lead was removed.

Table 2: Effect of polypyrrol synthesis conditions on lead separation

Polymer type	**Solvent**	**Additive material**	**Concentration of additives (gr/L)**	**Initial concentration of Lead (ppm)**	**Final concentration of Lead (ppm)**	**Percentage of Lead Removal (%)**
polypyrrol	water	-	-	50	41.90	16.21
polypyrrol	Acetonitrile			50	44.63	10.74
polypyrrol	Ethyl acetate	-	-	50	45.05	9.9
polypyrrol	Water+ Acetonitrile	-	-	50	44.05	11.9
polypyrrol	Water+ Ethyl acetate	-	-	50	44.58	10.84
polypyrrol	water	PVA	1.5	50	18.7	62.6
polypyrrol	Acetonitrile	PVA	1.5	50	43.95	12.1
polypyrrol	Ethyl acetate	PVA	1.5	50	45.85	8.31
polypyrrol	Water+ Acetonitrile	PVA	1.5	50	43.97	12.06
polypyrrol	Water +Ethyl acetate	PVA	1.5	50	45.04	9.93
polypyrrol	water	PEG	2	50	40.12	19.76
polypyrrol	water	PEG	4	50	36.64	26.73
polypyrrol	water	PEG	8	50	35.51	28.98
polypyrrol	water	PEG	16	50	34.75	30.5
polypyrrol	water	PEG	32	50	32.62	34.75
polypyrrol	water	PEG	64	50	34.43	31.14
Activated Carbon Powder				50	0.25	99.5

3-3- Nickel removal simulation by polypyrrol and its composites

According to Table 3 all polypyrroles have an unsatisfactory performance in nickel removal and the percentage of nickel removal by some polypyrroles is less than activated carbon with 14.96%

removal. Some polypyrroles also have a higher percentage of knockout than activated carbon, which does not seem very high in comparison with other heavy metals. Among polypyrrol and its composites, polypyrrol synthesized in water solvent and ferric chloride oxidant in the presence of polyethylene glycol as additive with concentration of 32 g/L with 23.14% removal had the highest percentage of nickel removal, the lowest nickel removal was related to polypyrrol composite and polyvinyl alcohol synthesized in acetonitrile by 0.25%.

Polyvinyl alcohol as an additive and surfactant has no positive effect on the efficiency of de-polypyrroles synthesized in water solvent and acetonitrile solvent and has not increased their capacity in nickel absorption. However, in ethyl acetate solvent, solvent+ mixture of ethyl acetate water with a volume ratio of 50.50 and acetonitrile + water mixture with a volume ratio of 50.50 polyvinyl alcohol had a positive effect and increased the percentage of nickel absorption. Polyethylene glycol as an additive has been able to positively affect the removal efficiency of nickel by polypyrrol and increase the removal capacity of nickel by polypyrrol. The optimum concentration of polyethylene glycol was 32 g/L. It can be stated that polypyrrol and its composites synthesized in different solvents are not suitable for nickel removal from aqueous environment. However, the most suitable polypyrrol composite is almost exclusive to polypyrrol and polyethylene glycol composites.

Table 3: Effect of polypyrrol synthesis conditions on Nickel separation

Polymer type	Solvent	Additive material	Concentration of additives (gr/L)	Initial concentration of nickel (ppm)	Final concentration of nickel (ppm)	Percentage of nickel Removal (%)
polypyrrol	water	-	-	50	49.15	1.71
polypyrrol	Acetonitrile			50	49.38	1.24
polypyrrol	Ethyl acetate	-	-	50	48.51	2.97
polypyrrol	Water+ Acetonitrile	-	-	50	47.78	4.45
polypyrrol	Water+ Ethyl acetate	-	-	50	46.14	7.73
polypyrrol	water	PVA	1.5	50	49.85	0.3
polypyrrol	Acetonitrile	PVA	1.5	50	49.88	0.25
polypyrrol	Ethyl acetate	PVA	1.5	50	47.75	4.5
polypyrrol	Water+ Acetonitrile	PVA	1.5	50	44.30	11.39
polypyrrol	Water +Ethyl acetate	PVA	1.5	50	42.25	15.5
polypyrrol	water	PEG	2	50	48.05	3.89
polypyrrol	water	PEG	4	50	47.57	4.85
polypyrrol	water	PEG	8	50	44.58	10.85
polypyrrol	water	PEG	16	50	42.12	15.75
polypyrrol	water	PEG	32	50	38.43	23.14
polypyrrol	water	PEG	64	50	42.56	14.88
Activated Carbon Powder				**50**	**42.52**	**14.96**

4-Conclusion

The main purpose of this study was to simulate the removal of heavy metals such as chromium, lead and nickel from aquatic environment by polypyrrol and its composites in the presence of different scenarios. According to the simulation, it can be found that all polypyrroles have good performance in the removal of +6 chromium and the percentage of chromium removal by all polypyrroles is higher than activated carbon. Among polypyrrol and its composites, polypyrrol synthesized in water solvent and ferric chloride oxidant in the presence of polyethylene glycol as additive had the highest percentage of chromium 6+ removal. However, all polypyrroles and their composites were unsuitable for lead and nickel removal and for removal of lead and cadmium, the removal percentage of polypyrrol and its composites was less than the percentage of lead and cadmium removal by activated carbon powder. Also, the percentage of nickel removal by some polypyrroles was lower than activated carbon with 14.96% removal. Some polypyrroles also have a higher percentage of knockout than activated carbon, which does not seem very high in comparison with other heavy metals. In general, it can be concluded that polypyrrol and its composites are suitable for removal of +6 chromium from aqueous environment, but are undesirable for removal of lead and nickel.

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