BIOACTIVE NANOCOMPOSITES BASED ON POLYPYRROLE AND POLYANILINE AS A HIGHLY EFFICIENT ADSORBENTS IN REMOVAL OF Pb AND Cd, USEABLE IN HOUSEHOLD WATER TREATMENT

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Abstract

The development of simple methods for the removal of heavy metal cations from water samples is an attractive field of research. In this regard, two novel magnetic tri-layer core-shell-shell bioactive nanocomposites, polypyrrole@polyxanthone triazole@Fe₃O₄(PPy@PXT@Fe₃O₄) and polyaniline@polyxanthone triazole@Fe₃O₄(PANI@PXT@Fe₃O₄) were prepared by a combination process involving click reaction and emulsion polymerization, successfully. Then, uptake of Pb(II) and Cd(II) from an aqueous solution by introduced materials was evaluated as a function of pH, adsorption dosage, contact time, and initial concentration of Pb(II) and Cd(II) through batch studies. The bioactive nanocomposites exhibited a high adsorption percentage 92.63 and 72.84 for Pb(II) and 90.66 and 93.70 for Cd(II) in optimized conditions, respectively.

Keywords and phrases: nanobioactive, ion removal, household water treatment, Pb(II), Cd(II).

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Isotherm and kinetic models showed that interactions of Pb(II) and Cd(II) with bioactive nanocomposites were in good agreement with the Freundlich isotherm and pseudo-second-order kinetic model. The maximum adsorption capacity (Q_m) of Pb(II) for two bioactive nanocomposites was 313 and 526mg/g, and in about Cd(II) was found 357 and 555.5mg/g, respectively. Hence, the introduced bioactive nanocomposites with high efficiency can be promising candidates for microorganism deactivator and risky ions removal in household water treatment.

1. Introduction

Today, water cleaning for the world's growing population is one of the major challenges. Heavy metals pollutants have developed a significant universal problem as they are not biodegradable and cannot be metabolized by the environment, so they endanger the environment and the health of human. These metal ions can be accumulated in living organisms and cause various diseases and disorders [1, 2].

Among heavy metal ions, lead and cadmium are known for its high priority toxicity [2, 3]. These heavy metal ions, when consumed above certain threshold concentrations can threaten the vital organs and cause various symptoms, such as central nervous system damage, liver disease, lung cancer, kidney damage, vomiting, and severe diarrhea. Besides that, in the case of cadmium, one of the initial signs of renal dysfunction is an increased urinary excretion of proteins [4, 5]. According to the World Health Organization (WHO) criteria, the permissible limits of lead and cadmium in wastewater are 0.015mg/L and 0.01mg/L, respectively [6].

So, it is necessary that they must be removed from the aqueous solution. Thus, reliable methods are needed to remove toxic metal ions from environmental and biological samples.

Among various methods for the removal of pollutants, such as adsorption [4, 5], reverse osmosis [7], chemical precipitation [8], nano-filtration [9], electro-ion exchange and coagulation [2], the adsorption is the most effective technique due to the availability of different adsorbents, design simplicity, low operational cost, easy handling and high efficiency that make it a potentially cost-effective method for the water refinement [10].

In the viewpoint of the adsorbent material, recently conductive polymers (CPs) such as polypyrrole (PPy), polyaniline (PANI), and polythiophene (PT) have been used effectually for the elimination of heavy metal ions from aqueous solutions by complexation [11, 12].

Moreover, in the case of these polymers in addition to mentioned property, antioxidant and antibacterial activity have put them in the spotlight [13, 14]. Their bioactivity beside the fantastic adsorption capability transformed them into the best bed for the fixed phase for water refinement. It is noteworthy that these polymers can destroy cell walls of bacteria and killed them and also can scavenge the radically and active species [15, 16].

It can be added to their unique properties, facility of synthesis and stability under several conditions [11, 12].

For more activity and observation of bio-synergic effect in CPs, it can prepare their composite with the other active material [13, 14]. In this project, this horizon is seen. Accordingly, xanthone bioactive derivative inserted on the polymer backbone by in situ click polymerization on the superparamagnetic nanoparticles as a core-shell component in the presence of Fe_3O_4 nanoparticles. In continuation, for putting the second shell on the prepared magnetic core-shell component, emulsion polymerization of pyrrole and/or aniline has been performed to afford corresponding core-shell-shell nanocomposite. Synthesis and characterization of the introduced materials have been done in details in some cases, such as NMR, FTIR, SEM, TEM, VSM, TGA, BET, conductivity, antioxidant activity, antibacterial activity and its capability in Pb(II) and Cd(II) removal has been evaluated.

Notable advantages of these nanocomposites are bioactivity, simple preparation, high efficacy and facility of separation of the nanocomposites from refined water by the magnet.

2. Experimental

Bioactive nanocomposites, PPy@PXT@Fe₃O₄ and PANI@PXT@Fe₃O₄, were prepared and characterized as illustrated in our previous works [13, 14]. Thermo Fisher scientific ICE 3300 atomic absorption spectrometer (AAS) was employed for determination of the metal ions.

Adsorption studies

Batch process was used for determining of Pb(II) and Cd(II) ions removal by super paramagnetic multilayers bioactive nanocomposites. Achieving to the optimum conditions were accomplished by altering the adsorbent dosage (10-40mg), pH (3, 6, and 10), initial concentration (20-100ppm) and contact time (1-24h). The solutions were shaken at 200rpm at room temperature.

Dilute solution of HCl or NaOH were used for the pH adjusting prior to the adsorption. Adsorption isotherms were studied with different initial concentrations of metal ions for the optimized amount of adsorbent (10mg). For the kinetic studies, the initial ion concentration was constant (20ppm) and the contact time was changed from 1 to 24h.

For error minimizing, each experiment was repeated three times and average results were reported. The concentration of metal ions was determined by using AAS. The obtained data in batch studies were used to calculate the percentage of ion removal by using the following equation:

$$R(\%) = \frac{C_i - C_f}{C_i} \times 100,$$

where C_i (mg/L) is the initial concentration of solution before sorption and C_f (mg/L) is the final concentration after the sorption of the ion.

The amount of metal adsorbed Q_e (mg/g), was determined by using the following mass balance relationship:

$$Q_e = \frac{C_i - C_e}{m} \times V,$$

where V is the volume of the solution (L); C_e (mg/L) is the equilibrium concentration, and m is the mass (g) of the adsorbent.

Adsorbent regeneration and reuse

Three following adsorption–desorption cycles were used to test the reusability of bioactive nanocomposite. Each adsorption process was carried out in a batch experiment for 24h. Then, the adsorbent was magnetically separated from the solution and then washed gently with distilled water to remove the left over solution. The collected adsorbent was then dispersed into 50mL of 0.1M HCl and shaken at 180rpm shortly for 30 min to regenerate the adsorbent. Prior to the next cycle, the generated adsorbent was washed repeatedly with distilled water until the effluent was neutral (pH = 7). The desorption percentage (D(%)) was calculated as follows:

$$D(\%) = \frac{A}{B} \times 100,$$

where A is the amount of Pb(II) and Cd(II) desorbed to the elution medium (mg) and B is the amount of Pb(II) and Cd(II) adsorbed on the adsorbent (mg).

Adsorption study of the Pb(II) and Cd(II)

As mentioned in the experimental section, for optimization of adsorption parameters some tests were done and the results are shown in Tables 1-4.

Table 1. Optimization of the adsorption parameters for Pb(II) sorption by PPy@PXT@Fe₃O₄

Pb(II) sorption							
Dosage (mg) ^a	R (%)	pH ^b	R (%)	C ₀ (ppm) ^c	R (%)	Time ^d (h)	R (%)
10	92.63	3	78.95	20	92.63	1	52.40
20	93.15	6	92.63	40	86.87	2	78.35
30	93.35	10	94.55	60	66.67	3	92.63
40	93.75	–	–	80	60.43	24	92.63
–	–	–	–	100	56.83	–	–
Isotherm and kinetics models							
Langmuir	Q _m = 313		K _L = 0.124		R ² = 0.94		
Freundlich	n = 2.97		K _F = 73.55		R ² = 0.95		
Pseudo first order	Q _e = 331		K ₁ = 0.03		R ² = 0.93		
Pseudo second order	Q _{e,cal} = 94.33, Q _{e,exp} = 104		K ₂ = 0.0004		R ² = 0.99		

^a(pH = 6, C₀ = 20ppm), ^b(dosage = 10mg, C₀ = 20ppm), ^c(dosage = 10mg, pH = 6),

^d(dosage = 10mg, pH = 6, C₀ = 20ppm). **The bold numbers are optimum values.**

Table 2. Optimization of the adsorption parameters for Cd(II) sorption PPy@PXT@Fe₃O₄

Cd(II) sorption							
Dosage (mg) ^a	R (%)	pH ^b	R (%)	C ₀ (ppm) ^c	R (%)	Time ^d (h)	R (%)
10	90.66	3	71.95	20	90.66	1	49.39
20	91.27	6	90.66	40	79.70	2	73.25
30	92.40	10	99.65	60	72.81	3	90.66
40	93.05	–	–	80	73.65	24	90.66
–	–	–	–	100	61.47	–	–
Isotherm and kinetics models							
Langmuir		Q _m = 357		K _L = 0.11		R ² = 0.94	
Freundlich		n = 2.54		K _F = 70.31		R ² = 0.99	
Pseudo first order		Q _e = 537		K ₁ = 0.032		R ² = 0.87	
Pseudo second order		Q _{e,cal} = 102.04, Q _{e,exp} = 121		K ₂ = 0.0002		R ² = 0.99	

^a(pH = 6, C₀ = 20ppm), ^b(dosage = 10mg, C₀ = 20ppm), ^c(dosage = 10mg, pH = 6),

^d(dosage = 10mg, pH = 6, C₀ = 20ppm). **The bold numbers are optimum values.**

Table 3. Optimization of the adsorption parameters for Pb(II) sorption by PANI@PXT@Fe₃O₄

Dosage (mg) ^a	R (%)	pH ^b	R (%)	C ₀ (ppm) ^c	R (%)	Time ^d (h)	R (%)
10	72.84	3	56.25	20	72.84	1	36.82
20	73.93	6	72.84	40	61.02	2	56.60
30	76.09	10	93.85	60	57.85	3	72.84
40	78.01	–	–	80	59.31	24	72.84
–	–	–	–	100	56.83	–	–
Isotherm and kinetics models							
Langmuir	Q _m = 526			K _L = 0.026		R ² = 0.94	
Freundlich	n = 1.5			K _F = 23.19		R ² = 0.95	
Pseudo first order	Q _e = 301			K ₁ = 0.029		R ² = 0.90	
Pseudo second order	Q _{e,cal} = 74.62, Q _{e,exp} = 88.09			K ₂ = 0.0003		R ² = 0.99	

^a(pH = 6, C₀ = 20ppm), ^b(dosage = 10mg, C₀ = 20ppm), ^c(dosage = 10mg, pH = 6),

^d(dosage = 10mg, pH = 6, C₀ = 20ppm). **The bold numbers are optimum values.**

Table 4. Optimization of the adsorption parameters for Cd(II) sorption PANI@PXT@Fe₃O₄

Dosage (mg) ^a	R (%)	pH ^b	R (%)	C ₀ (ppm) ^c	R (%)	Time ^d (h)	R (%)
10	93.70	3	98.23	20	93.70	1	51.20
20	94.45	6	93.70	40	81.22	2	73.20
30	94.65	10	99.71	60	68.63	3	93.70
40	95.25	–	–	80	53.21	24	93.70
–	–	–	–	100	51.19	–	–
Isotherm and kinetics models							
Langmuir	Q _m = 555.5			K _L = 0.082		R ² = 0.93	
Freundlich	n = 2.26			K _F = 82.22		R ² = 0.99	
Pseudo first order	Q _e = 398			K ₁ = 0.031		R ² = 0.89	
Pseudo second order	Q _{e,cal} = 96.15, Q _{e,exp} = 109.54			K ₂ = 0.0003		R ² = 0.99	

^a(pH = 6, C₀ = 20ppm), ^b(dosage = 10mg, C₀ = 20ppm), ^c(dosage = 10mg, pH = 6),

^d(dosage = 10mg, pH = 6, C₀ = 20ppm). **The bold numbers are optimum values.**

3. Result and Discussion

According to today's need of world people to fresh and clean water, plenty of works focused on water cleaning [17, 18]. Wastewater which was drained from industrial companies to sluice water can poison the water for human and animals. So, the attempts are running to decrease and omit the harmful contents of water [19].

In this regard, many adsorbents introduced to resolve this problem. As is clear, in addition to the heavy metal ions that are high risk for human health, water microorganisms can threat people life. Some of the microorganisms are killer and dangerous, hence confront them is important as well as heavy metal ions [20]. Also, the presence of oxidative active material and stable free radicals in drinking water is another problem which can cause the dangerous diseases and different kinds of cancer [21]. Summation of these problems give bad feels to people that water which is the main factor for the living, maybe not suitable for drinking [22]. But, good researches have been done on water treatment to resolve these problems. Many of the introduced materials have not the capability of ion adsorbent, antibacterial and antioxidant activity, simultaneously. However, production of the materials which supply all of these capabilities together must be very important and world-shaking. Accordingly, we focused on the preparation of novel bioactive nanocomposites that have all of the noted properties. Its surprising antioxidant and antibacterial activities that mentioned in our previous works [13, 14], encouraged us to evaluate its ion removal ability (Scheme 1). For both bioactive nanocomposites similar conditions were applied to compare the capability of the prepared nanoadsorbents, together.

Scheme 1. Schematic explanation of the synthetic pathway and activity studying.

Effect of adsorbent dosage

Four doses, 10, 20, 30, 40mg of bioactive nanocomposites were applied in removal tests in which 10mg of adsorbent was selected as the best option for both. Because no significant changes were observed in adsorption efficiency by altering dose amounts.

pH effect on the adsorption

The pHs 3, 6 and 10 were considered for adsorption tests. According to the pH evaluation, acidic pH because of protonation of CPs backbone, hydroxyl, NH, and nitrogen atoms of triazole rings and presence of electrostatic repulsion, has low adsorption efficiency. In contrast to basic pH, the increment of adsorption is due to activation of adsorbent sites

and also hydroxides of metal ion that are insoluble may precipitate and electrostatic attraction increase adsorption efficiency. Finally, pH = 6 was applied as optimized pH, since adsorption was satisfied and no interferences were observed.

Initial concentration

20, 40, 60, 80, and 100ppm were tested concentrations. According to adsorption efficiency, 20ppm was the best choice. Reduction of adsorption efficiency by the increase of concentration is probably due to saturation of active sites by adsorbed ions.

Optimum contact time

Based on the experiments, between 1 to 24h as contact times, 3h was the end of the adsorption process. Because after that adsorption efficiency remained stable. Fixation of adsorption efficiency is maybe also due to saturation of adsorbent sites.

Adsorption isotherms

For designation adsorption mechanism, Langmuir, Freundlich, pseudo-first and second order isotherms were studied in this work. The Langmuir isotherm theory is often used to describe the equilibrium adsorption isotherms of the homogeneous system [23]. The non-linear equation of Langmuir isotherm model is expressed as:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m},$$

where C_e and Q_e are the equilibrium concentration (mg/L) and equilibrium adsorption capacity (mg/g), respectively. Q_m is the maximum metal ion adsorption capacity (mg/g), and K_L is the Langmuir constant related to the adsorption energy (L/mg). The isotherm constants were calculated from the linear plot between C_e / Q_e and C_e .

The Freundlich model that is the oldest equation describes the adsorption of a reversible heterogeneous surface and is not limited to a monolayer adsorption capacity. This model mentions that the sorption energy decreases exponentially from the center of adsorbent [23]. The Freundlich equation is:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e,$$

where K_F is a constant related to the adsorption capacity and $1/n$ is an experimental parameter related to the adsorption intensity, which defines the affinity of the process to be a chemisorption ($n < 1$) or a physisorption ($n > 1$). The Q_e and C_e were already mentioned.

According to the found data, ions adsorption have the good fitting with every two isotherms ($R^2 \geq 0.94$). In the comparison of two Freundlich isotherms for ions removal, it was found that both ion removals are physisorption ($n = 2.97, 1.5$ for Pb(II) and $n = 2.54, 2.26$ for Cd(II)).

The kinetic models, pseudo-first-order, pseudo-second order, models were used to investigate the kinetics involved in the adsorption of the selected heavy metal ions by the superparamagnetic bioactive nanocomposite. The pseudo-first-order kinetic model is valid only for the initial adsorption period and was suggested for the adsorption of solid/liquid systems [24]:

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_1}{2.303} t,$$

where Q_e and Q_t are the adsorption capacity (mg.g^{-1}) on the beads at the equilibrium and at time t , respectively. $K_1(\text{min}^{-1})$ is the rate constant which can be obtained from $\log(Q_e - Q_t)$ versus t . The pseudo-second-order model is given as [24]:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e} t,$$

where $K_2(\text{g mg}^{-1} \text{ min}^{-1})$ is the rate constant. This model is used for predicting the kinetic behaviour of chemical sorption as a rate controlling step. The K_2 and Q_e can be determined from the intercept and slope of the plot of t / Q_t versus t , respectively.

According to reported literatures about Pb(II) and Cd(II) removal on the basis of their adsorption capacity (Q_m), it is understandable which the introduced materials in the present work have much higher activity than the others (Table 5).

Table 5. Adsorption capacities of different adsorbents in up taking of Cd(II) and Pb(II) ions

Metal ion	Adsorbent type	Q_m (mg/g)	Ref.
Pb(II)	PPy@PXT@Fe ₃ O ₄ , PANI@PXT@Fe ₃ O ₄	313, 526	Present work
Cd(II)	PPy@PXT@Fe ₃ O ₄ , PANI@PXT@Fe ₃ O ₄	357, 555.5	Present work
Pb(II)	Magnetic bio-sorbent hydrogel	88.49	[10]
Pb(II)	PGMA-MAn copolymer@Fe ₃ O ₄	101.01	[5]
Cd(II)		121.95	
Cd(II)	PEI-grafted magnetic porous powder	105.26	[25]
Pb(II)	Poly (aniline-co-3-aminobenzoic acid)	81.43	[12]
	Poly (aniline-co-3-aminobenzoic acid) @Fe ₃ O ₄	138.31	
Cd(II)	Manganese oxide	104.17	[26]
Pb(II)	Chitosan-abrus precatorius blended beads	161.3	[27]
Cd(II)		108.6	
Pb(II)	Amino	57.74	[28]
Cd(II)	Functionalized mesoporous and nano mesoporous silica	18.25	
Cd(II)	Nanocomposite based on poly (xanthoneamide-triazole-ethercalix) and TiO ₂ nanoparticles	208.33	[4]
Pb(II)	Sol-gel derived inorganic oxide adsorbent	102.02	[29]
Cd(II)		94.05	

According to the data from Table 5, it is comprehensible that the introduced materials have very high quality for ion removal. Moreover, these material have impressive bioactivity to degrade the bacterias and scavenge the active radical and oxidative material that are threaten factors for healthy life. In comparison of bioactive nanocomposites in the present work, it is clear that the PPy@PXT@Fe₃O₄ has bioactivity

effects more than PANI@PXT@Fe₃O₄, but its ion removability is lesser. Generally, it is concluded that PANI based nanocomposite has improved ion removability while PPy nanocomposite showed higher bioactivity.

Desorption and reusability of the adsorbents

It is important to regenerate and restore the used adsorbent after adsorption process. For this purpose, desorption experiments were carried out in the diluted HCl solution for 30 min. Three consecutive adsorption/desorption cycles were conducted under the same conditions. The adsorption efficacy of the PPy@PXT@Fe₃O₄ and PANI@PXT@Fe₃O₄ decreased 3.25-2.89% for Pb(II) and 2.15-1.89% for Cd(II) after three cycles of intensive desorption process, while desorption decreased about 8-7.5% and 6-5.3% for Pb(II) and Cd(II), respectively.

It is noteworthy that adsorption ability of the magnetic adsorbents have no significant changes after three cycles even though desorption steps were not complete.

Moreover, leaching out of Fe ions during recovery process and antibacterial activity decrement were ignorable, while antioxidant activity decreased about 5 and 6.5%, respectively, that it seems be due to coordination of active sites with heavy metals and the slight destruction of the bioactive nanocomposites.

4. Conclusion

In the present work, capability of the novel bioactive supermagnetic nanoadsorbents were evaluated in the removal of Pb(II) and Cd(II) as high-risk heavy metal ions. These bioactive nanocomposites are the wonderful adsorbent because they have three properties concertedly. First and second properties that had raised in previous work [13, 14] and the third property that was ion removal has shown in this work. As you know household water treatment have different filters that work separately for some aims, but they are a good position for association and

living of microorganisms. Therefore, they may have good performance in ion and dye removal but can increase some diseases arising from their microorganisms. So, design and construction of new filters that have antioxidant and antibacterial activity moreover than ion removal capability, are very necessary. Our attempts were in this regard to design and construct the new materials which are efficient in both fields. With a general look, it is comprehensible that introduced bioactive nanocomposites are effective in the water treatment and are a good candidate for using in the household water treatment apparatus.

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