

Polyaniline Modified with Cobalt-Hexacyanoferrate (PmCH) as an Adsorbent for Removal of Heavy Metals from Aqueous Solutions

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Abstract. In this study, polyaniline modified with cobalt-hexacyanoferrate (PmCH) composite was synthesized and characterized for removal of Rb^+ , Cd^{2+} , Zn^{2+} , Pb^{2+} , and Ni^{2+} by FTIR and XRD. The effect of pH, adsorbent dosage, ionic strength, contact time, initial ion concentration, and temperature were studied. The competition adsorption experiments between metal ions were investigated. Batch desorption was also conducted to evaluate the reusability of PmCH. The maximum adsorption capacities were 96.15, 27.17, 17.85, 19.15, and 4.76 mg g^{-1} of Rb^+ , Cd^{2+} , Zn^{2+} , Pb^{2+} , and Ni^{2+} , respectively. The optimum pH was determined at natural pH of each solution.

1 Introduction

As water pollutants, heavy metals have come up as an interesting area of water research [1]. One of the most popular techniques to removal of these toxic compounds is adsorption process [2]. Due to strong adsorption capability to removal of metal ions, polyaniline can be used as a good prospect for adsorption applications [3]. On the other hands, cobalt-hexacyanoferrate is considered as an effective compound in ion exchange and storage potential of counter cations [4]. In this study, polyaniline modified with cobalt-hexacyanoferrate (PmCH) composite was prepared and characterized for removal of Rb^+ , Cd^{2+} , Zn^{2+} , Pb^{2+} , and Ni^{2+} from aqueous solutions.

2 Materials and Methods

2.1 Chemicals and instrumentations

$\text{Ni}(\text{NO}_3)_2$, cobalt (II) chloride hexahydrate, aniline, HCl, KOH, ammonium peroxydisulfate, $\text{Pb}(\text{NO}_3)_2$, ZnCl_2 , $\text{Cd}(\text{NO}_3)_2$, and RbCl were used in analytical grade (Germany, Merk). FTIR (Bruker, Vector 22) and XRD (STOE, STIDY-MP, Germany) measurements were performed to detect the morphological studies of polyaniline and PmCH. The ion concentrations were analyzed using an ICP-OES (Optima 7300 DV, Perkin Elmer).

Nomenclature	
V	Solution volume
C_i / C_e	Initial / Equilibrium concentration of metal ion
W	Adsorbent weight
q_e / q_t	Adsorption capacity at equilibrium / at any time
k_1 / k_2	The rate constant of pseudo-first-order / pseudo-second-order adsorption
h	The initial adsorption rate
k_f / k_L	The Freundlich constant / Langmuir constant
n	Adsorption intensity and bond energy (Freundlich isotherm)

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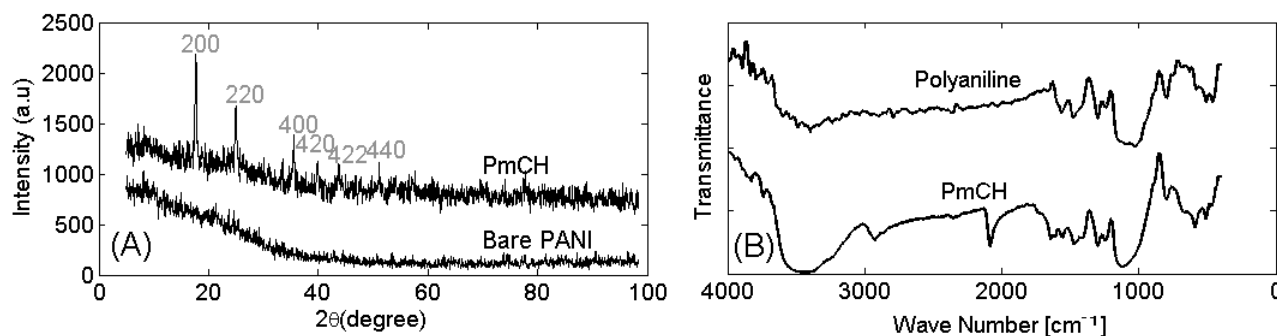


Figure 1. Characterization of polyaniline and PmCH by (A) XRD (B) FTIR.

2.2 Synthesis of Polyaniline

Ammonium peroxydisulfate (one gram) was dissolved in 100 mL of 1 mol L⁻¹ HCl media. After 30 min, one millilitre of aniline was dropwise added to form a dark green solution. After 5 h of continuous stirring, the solution was filtered and its precipitate was collected. Then, the precipitate was finally washed and dried with distilled water.

2.3 Synthesis of PmCH

Cobalt (II) chloride hexahydrate (2 mol L⁻¹), potassium ferricyanide (3 mol L⁻¹), and ammonium peroxydisulfate (one gram) were dissolved in 100 mL of 1 mol L⁻¹ HCl. After 30 min, one millilitre of aniline was dropwise added to form a dark green solution. After 5 h of continuous stirring, the solution was filtered and its dry precipitate was collected. Then, the precipitate was finally washed and dried with distilled water at room temperature.

2.4 Adsorption and desorption of heavy metal ions

In general, one gram of dry adsorbent was added to 100 mL of solutions containing Rb⁺, Cd²⁺, Zn²⁺, Pb²⁺, and Ni²⁺ ions. These solutions were shaken in a thermostatic shaker. The initial pH of solution for each ion was adjusted in the range of 2.5 to 9. In order to evaluate the effects of concentration of heavy metals, the initial concentration of the solutions were considered between 10-100 mg L⁻¹. The adsorbent dosage was considered at 3.5 gr L⁻¹. The adsorption capacity and ion removal were calculated by [2]:

$$q_e = \frac{C_i - C_e}{W} \times V \quad ; \quad \text{removal}(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

3 Equations and mathematics

3.1 Characterization of Polyaniline and PmCH

The XRD patterns of polyaniline and PmCH are depicted in figure 1A which illustrates that polyaniline and PmCH have an amorphous and the cubic structures, respectively. The reflections of PmCH at 200, 220, 400, 420, 422, and 440 were located at 18, 24.8, 35.5, 40.0, 43.9, and 51.0°, respectively (JCPDS 5-0036, 5-0037). The changes in FTIR spectra of polyaniline and PmCH at 2090 cm⁻¹ (Fe-CN-Co) indicates that cobalt-hexacyanoferrate have been successfully added to the polyaniline; see figure 1B. The bands at 788, 1105, 1286, 1444, and 1610 cm⁻¹ correspond to C-H bending, C-N bonds in the benzenoid rings, C-N bonds in the quinoid rings, benzenoid rings, and quinoid rings, respectively [2]. A broad band at around 3100–3650 and 2850–2950 cm⁻¹ are assigned to O-H stretching for the hydrogen bonded hydroxyl groups and the alkyl stretching groups, respectively [3].

3.2 Effect of pH

The effects of initial pH on the adsorption of each metal ion onto PmCH were evaluated at pH 2-6 and an initial ion concentration of 100 mg L⁻¹. As can be seen in figure 2A, adsorption capacity of PmCH was enhanced with increasing the pH. At low pH, the surface of PmCH has a positive charge. The negative charge density of PmCH surface was increasing with increasing the pH. At pH above the zero point charge, the functional groups of PmCH surface have the negative charge; hence, maximum cation sorption occurs at high pH [5]. At high pH, due to salt formation of Cd²⁺, Zn²⁺, Pb²⁺, and Ni²⁺ some precipitations were appeared. So, these studies do not continued more than precipitations pH. Fortunately, the optimum pH was determined at natural pH of each solution.

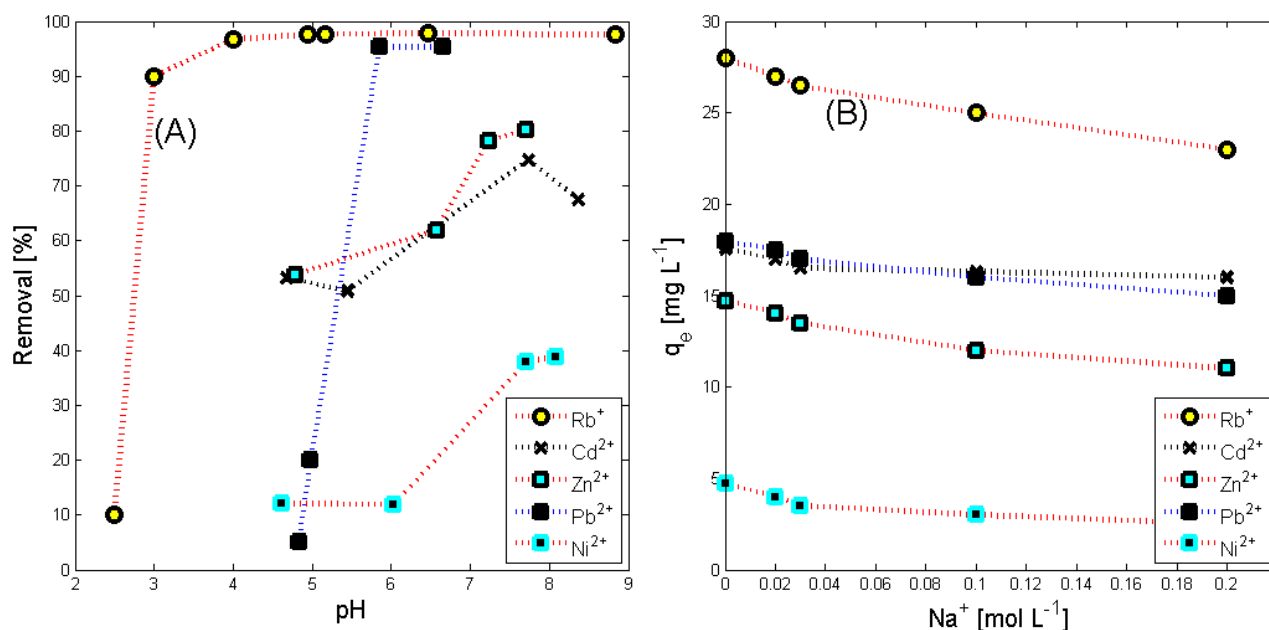


Figure 2. Effect of (A) pH (B) ionic strength (initial concentration: 100 mg L⁻¹).

3.3 Effects of ionic strength

The effect of ionic strength was evaluated by adding five different concentrations of NaNO₃ at 100 mg L⁻¹ of initial metal concentration; see figure 2B. NaNO₃ as an inorganic salt plays an important roles in aqueous solution. The adsorption of metal ion on PmCH was decreased with a raise of NaNO₃ concentration due to performance of salt screens as an electrostatic interaction factor of the opposite charges between metal ions and PmCH surface [1].

3.4 Effects of contact time and adsorption kinetics

The effect of contact time between each ion and PmCH was studied at 3.5 g L⁻¹ PmCH dosage and 100 mg L⁻¹ ion concentration, which illustrated that the adsorption of ion was as a function of contact time. The pseudo-first-order (equation 2) and the pseudo-second-order kinetic (equation 3) models have been applied to determine and describe the kinetic process of liquid-solid phase [2]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

$$(t/q_t) = (1/k_2 q_e^2) + (t/q_e) \quad ; \quad h = k_2 q_e^2 \quad (3)$$

Studies showed that more than 90% of the total adsorption occurs within the first 100-150 min and the concentration approached their equilibrium value at 200-400 min, which can be confirmed by h value in Table 1. The initial adsorbent rate of Rb⁺ was clearly more than the others. By comparing the correlation coefficient R², it appears that the pseudo-second-order kinetic fits the experimental data more accurately than the pseudo-first-order kinetic. This model suggests that ions are exchanged with hydrogen on the PmCH surface [3].

3.5 Equilibrium studies in single-component system

The effect of initial concentrations of each ion was carried out using Langmuir (equation 4) and Freundlich (equation 5) models within range of 10-100 mg L⁻¹ of ions at 25°C [5]:

$$(C_e/q_e) = (1/q_{\max} k_L) + (C_e/q_{\max}) \quad (4)$$

$$\log q_e = \log k_f + (1/n) \log C_e \quad (5)$$

The adsorption capacities were increased with increasing

Table 1. The kinetics parameters for adsorption of ions using PmCH.

Ion	q _e [mg g ⁻¹]	Pseudo-second-order			Pseudo-first-order	
		k ₂ [g mg ⁻¹ min ⁻¹]	h [mg g ⁻¹ min ⁻¹]	R ²	k ₁ [min ⁻¹]	R ²
Rb ⁺	96.15	0.0008	0.6803	0.997	0.0076	0.903
Cd ²⁺	27.17	0.0005	0.1786	0.979	0.0070	0.980
Zn ²⁺	17.85	0.0007	0.1786	0.989	0.0047	0.971
Pb ²⁺	19.15	0.0009	0.3199	0.995	0.0041	0.949
Ni ²⁺	4.76	0.0015	0.0381	0.984	0.0068	0.990

the initial concentration of each ion. q_{\max} , k_L , k_f , and n parameters were calculated from the slope and intercept of the above equations plots. The correlation coefficient (R^2) of Langmuir model (for all of ions were in the range of 0.992-0.998) fits the experimental data better than that of Freundlich isotherm (for all of ions were in the range of 0.819-0.965) which indicates that PmCH has a homogeneous surface, with equal energy in its activate sites. The maximum adsorption capacities were 96.15, 27.17, 17.85, 19.15, and 4.76 mg g⁻¹ of Rb⁺, Cd²⁺, Zn²⁺, Pb²⁺, and Ni²⁺, respectively. The k_L parameters were 0.176, 0.064, 0.110, 0.515, and 0.212 L mg⁻¹ of Rb⁺, Cd²⁺, Zn²⁺, Pb²⁺, and Ni²⁺, respectively.

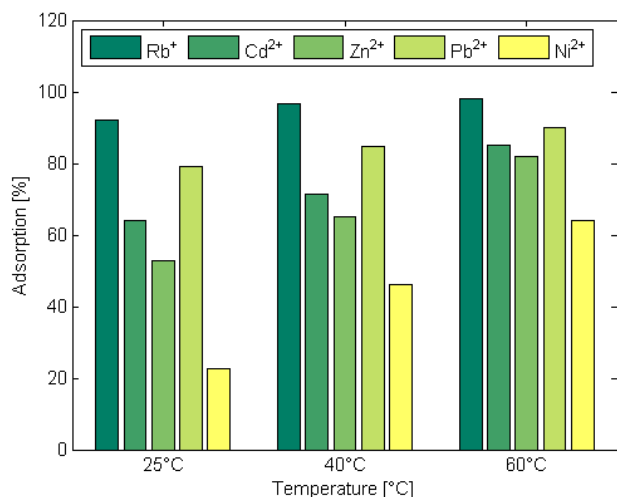


Figure 3. Effect of temperature at 25, 40, and 60 °C (initial concentration: 100 mg L⁻¹).

3.6 Effects of temperature

The effects of temperature on the adsorption of heavy

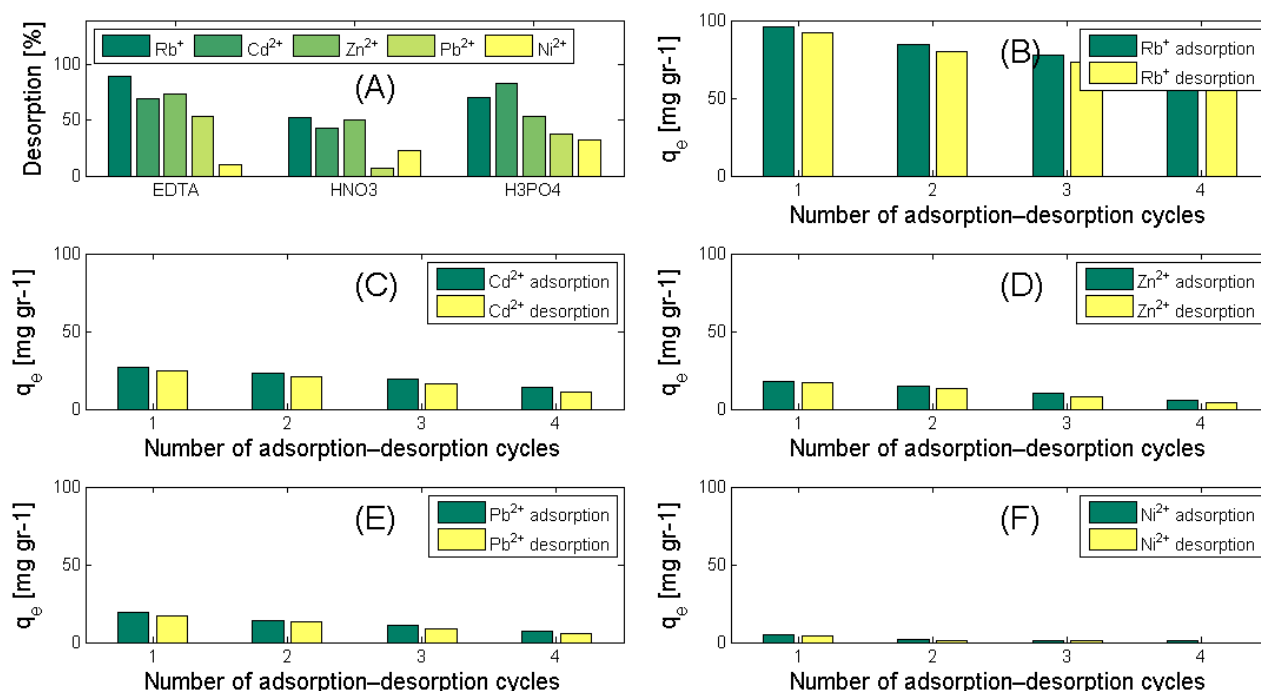


Figure 4. Effect (A) Desorption percentage of ions from PmCH using three different buffers. Adsorption-desorption cycles of PmCH for (B) Rb⁺-EDTA, (C) Cd²⁺-H₃PO₄, (D) Zn²⁺-EDTA, (E) Pb²⁺-EDTA, and (F) Ni²⁺-H₃PO₄.

metals onto PmCH were evaluated at three different temperatures (25, 40, and 60 °C) and 100 mg L⁻¹ of initial metal concentration; see figure 3. The adsorption capacity of each heavy metal onto PmCH was increased with increasing the temperature, which indicates that the adsorption of heavy metals onto PmCH is endothermic process.

Enhance of adsorption capacity with increasing the temperature is due to the strengthening of adsorptive forces between the adjacent molecules of the adsorbed phase, and between the ion species and active sites of the PmCH.

3.7 Multi-component adsorption (in binary mixtures)

To determine the competitive effect of ions on each other in binary mixture, removal percentage of 1st ion are shown in Table 2 at 3.5 g L⁻¹ PmCH dosage and 100 mg L⁻¹ ion concentration. The removal percentage of Rb⁺ (as the 1st ion) in the presence of Cd²⁺, Zn²⁺, Pb²⁺, and Ni²⁺ (as the 2nd ion) were 84.3, 89.7, 84.1, and 91.5 percent. However, the removal percentage of Cd²⁺, Zn²⁺, Pb²⁺, and Ni²⁺ (as the 1st ion) in the presence of Rb⁺ (as the 2nd ion) were 32.1, 22.1, 46.7, and 9.3 percent. These results illustrate that Rb⁺ was more to be adsorbed onto PmCH even in binary mixture. The rank of removal efficiency in binary mixtures was Rb⁺ > Pb²⁺ > Cd²⁺ > Zn²⁺ > Ni²⁺ which can be explained by Lewis acids low and classification of heavy metals in metal into class-B ‘soft ions’, class-A ‘hard ions’ and borderline ions [1]. Rb⁺, Cd²⁺, Pb²⁺, Zn²⁺ and Ni²⁺ on the basis of the Lewis acids low are classified in A, B, B, borderline, and borderline, respectively [6].

Table 2. PmCH Removal percentage based on 1st ion removal in binary mixtures at 25°C.

1st ion	2nd ion				
	Rb ⁺	Cd ²⁺	Zn ²⁺	Pb ²⁺	Ni ²⁺
Rb ⁺	-	84.3	89.7	84.1	91.5
Cd ²⁺	32.1	-	54.4	48.0	59.3
Zn ²⁺	22.1	39.4	-	36.5	48.2
Pb ²⁺	46.7	53.5	68.2	-	75.3
Ni ²⁺	9.3	9.9	16.4	6.8	-

3.8 Desorption and reusability

Desorption studies of metal ions were carried out to evaluate the reusability of PmCH using three different buffers (EDTA, HNO₃, and H₃PO₄); see figure 4. The best buffers for excellent desorption efficiency for Rb⁺, Cd²⁺, Zn²⁺, Pb²⁺, and Ni²⁺ ions were EDTA, H₃PO₄, EDTA, EDTA, H₃PO₄, respectively (figure 4A). The coordination ligands of each buffer formed a strong bonding with a selective ion, when each buffer was added to the ion adsorbed-PmCH. Ion–ligand bonding Strength was the determining factor for making more easily desorb from the PmCH. The reusability of PmCH using the selective buffer for each ion by following four cycles of adsorption–desorption process was shown in figure 4B–F. The negligible changes of adsorption–desorption cycles indicate that PmCH is an adsorbent with no irreversible sites and can be used as a reusable adsorbent in wastewater treatment.

4 Conclusions

PmCH was synthesized and characterized for removal of heavy metals by FTIR and XRD. The adsorption of metal ion was decreased with a raise of NaNO₃ concentration. The Langmuir isotherm and pseudo-second-order kinetic models fit the experimental data better than the others. The maximum adsorption capacities were 96.15, 27.17, 17.85, 19.15, and 4.76 mg g⁻¹ of Rb⁺, Cd²⁺, Zn²⁺, Pb²⁺, and Ni²⁺, respectively. The adsorption capacity of each ion was increased with increasing the temperature. The rank of removal efficiency in binary mixtures was Rb⁺ > Pb²⁺ > Cd²⁺ > Zn²⁺ > Ni²⁺. The best buffers for excellent desorption efficiency for Rb⁺, Cd²⁺, Zn²⁺, Pb²⁺, and Ni²⁺ ions were EDTA, H₃PO₄, EDTA, EDTA, H₃PO₄, respectively.

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