

Adsorption Studies of Cd(II) and Zn(II) onto Polypyrrole/ Sb₂O₃ Nanocomposite: Kinetics, Equilibrium, and Thermodynamics

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Abstract

Introduction: Heavy metal ions are very toxic to public and personal health. A special polypyrrole with environmental stability and reusability was used to remove metal ions from aqueous solution. In this work, a new polypyrrole (PPy/Sb₂O₃) nanosorbent was successfully synthesized in aqueous solution.

Methods: The purpose of this research was to investigate the adsorption properties of polypyrrole nanocomposites for the removal of Cd(II) and Zn(II) from aqueous solution. Batch various factors affecting the adsorption equilibrium were investigated in detail. Also, different models (isotherm, kinetic, and thermodynamic) were compared to describe the adsorption phenomenon.

Results: The adsorption isotherms for Cd(II) and Zn(II) were well fitted by the Langmuir model with a maximum monolayer capacity of 17.33 and 15.361 mg/g, respectively, for Cd (II) and Zn (II) ions. Moreover, thermodynamic analysis shows the endothermic nature and spontaneity of the adsorption process with increasing entropy in PPy-PVA/Sb₂O₃. From the kinetic results, it was concluded that the pseudo-second-order kinetic model is the best in describing the adsorption process for Cd (II) and Zn (II). The consistency of the experimental q_e with the q_e calculated from the pseudo-second-order kinetic model indicated that the adsorption of Cd(II) and Zn(II) on PPy-PVA/Sb₂O₃ is probably controlled by chemisorption.

Conclusion: This study shows that polypyrrole and its nanocomposites have a potential for use as effective adsorbents due to their ease of synthesis, low cost, and regeneration efficiency for the removal of heavy metal ions from aqueous solutions.

Keywords: Polypyrrole, Adsorption, Nanocomposite, Isotherm, Thermodynamic

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Introduction

Water pollution by various pollutants such as heavy metal ions, paints, oils, pharmaceuticals, and nutrients is one of the most important environmental and health problems. Heavy metal ions such as iron, lead, chromium, cobalt, zinc, arsenic, copper, nickel, mercury, and cadmium are among the persistent pollutants in wastewater (1-3). The release of heavy metals in the environment, which is mainly caused by human activities, even at low concentrations due to high solubility in water and soil, high toxicity, and non-biodegradable nature, causes dangerous effects on

plants, animals, and living organisms (4,5). It also causes bioaccumulation and biomagnification in the food chain. Heavy metals such as Cd(II) and Zn(II) exposure causes serious health effects, including cancer, organ damage, nervous system damage, lung damage, damage to the brain, and eventually leads to death. Therefore, the heavy metal ions in wastewater should be removed before the water is discharged into the environment.

To remove heavy metals from the contaminated wastewater, various treatment approaches such as ion-exchange (6), coagulation-flocculation (7), physical



and chemical precipitation (8), membrane filtration (9), electrochemical treatment (10), reverse osmosis (11) and adsorption processes (12) have been employed. Most of these methods are effective but require large amounts of chemicals and high energy. Among the approaches, absorption technology is the best method in wastewater treatment due to its significant advantages, including cheap materials, availability, ease of use, and high efficiency compared to other conventional methods (13-15). To achieve high absorption efficiency in wastewater, special attention should be paid to the design and synthesis of adsorbents with high absorption capacity (16-18). Recent studies have focused on many interesting adsorbents such as fly ash (19), graphene oxide and reduced graphene oxide (20), inorganic minerals (21), active carbon (22), zeolites (23), and biosorbents (24). However, most of these adsorbents have weaknesses such as low adsorption capacity and slow kinetics, difficulty separating after purification, and low surface area. Therefore, finding new adsorbents with high adsorption performance is still challenging (25). Recently, conducting polymers such as polyaniline (PANi), polypyrrole (PPy), and polythiophene (PTh) with interesting stability and doping capabilities have been introduced as adsorbents for the adsorption of heavy metal ions from aqueous solutions (26,27). Their availability, easy preparation, and performance make them desirable in many applications. Among conductive polymers, polypyrrole (PPy) is one of the most frequently studied polymers, which has many advantages including non-toxicity, good biocompatibility, easy synthesis, high environmental stability, low cost, and ion exchange properties (28). In polymer chains, PPy has positively charged nitrogen atoms that may easily bind heavy metal ions (29). There are various methods for the synthesis of conducting polymers, among which the in-situ polymerization method is of particular importance. The advantages of this method include the ability to produce polymer products with the required properties and characteristics by adjusting the process conditions, ease of carrying out the process, reducing waste and production costs, and reducing production time (30).

Therefore, in the present study, it has been tried to use chemically modified polypyrrole with antimony oxide (PPy/Sb₂O₃) in the presence of poly(vinyl alcohol) to remove Cd(II) and Zn(II) ions from water. The batch equilibrium method was used to study the adsorption process. PPy/Sb₂O₃ composites were analyzed by FTIR, XRD, and SEM. Factors affecting the absorption process, such as pH, time, and temperature, were investigated. Also, based on the experimental results, adsorption kinetics, equilibrium, and thermodynamics were discussed.

Materials and Methods

Instrumentation

A digital scale model D-500, pH meter model HANA211, centrifuge model Z36HK, Fourier transform infrared (FTIR) spectrometer (Avatar 370, Nicolet, USA) within the 400-4000 cm⁻¹ range, X-ray diffraction (XRD) with Cu

K α radiation (X'Pert Pro, Panalytical, Netherlands), flame atomic absorption spectrophotometer model Thermo electrene, scanning electron microscope (SEM) model KYKYEM3200, oven Binder model FD 23 and magnetic mixer model MK20 (Germany) were employed.

Materials

Materials used in this study were monomer of pyrrole (d=0.97 g/cm³) from Aldrich, poly(vinyl alcohol) (PVA), ferric chloride, and antimony oxide (Sb₂O₃), which were obtained from Merck (Germany). All reagents were used as received. During this research, deionized water was used, and pyrrole monomers were purified using distillation.

Synthesis of polypyrrole/Sb₂O₃ in the presence of PVA

An in situ chemical polymerization method was used to prepare the nanosorbent. For the synthesis, 5 g of FeCl₃ was added to 50 mL distilled water. 0.2 g of PVA and 1.0 g of Sb₂O₃ were dissolved in 50 mL distilled water; a uniform solution was achieved using a magnetic mixer for 30 min and added to the oxidant solution. Finally, 1 mL of pyrrole monomer was added to a stirred aqueous solution, which was maintained under constant stirring. The reaction was carried out for 5 h at room temperature. The product was collected by filtration. To separate the oligomers and impurities, the product was washed several times with deionized water. It was then dried at about 60°C in an oven for 24 h. A pure PPy was synthesized using the same method used previously, without Sb₂O₃ and PVA (100 mL distilled water containing 5 g FeCl₃ and 1 mL pyrrole monomer).

Batch adsorption experiment

Adsorption experiments in this study were conducted to investigate the effects of experimental conditions on the adsorption of Cd(II) and Zn(II) and to determine the conditions that obtain the maximum removal of metal ions. The standard heavy metal solutions used in the study were prepared from CdCl₂ and Zn(NO₃)₂, respectively, with deionized water. The pH values of the solution in these experiments were approximately 2-7. To determine the amount of removal of metal ions by nanocomposites, the solution of metal ions (50 mg/L) was mixed with 0.3 g of powder adsorbent. 30 mL of heavy metal solution was placed in a shaker at a speed of 400 rpm for 45 minutes to carry out the adsorption process. At the end of the process, the adsorbent was filtered. The amount of metal ions in the solution after the adsorption process was measured by atomic absorption. All experiments were performed twice to obtain average values. The deviation of this method was less than 5%. The pH of the solution was adjusted using 0.1 mol/L NaOH and 0.1 mol/L HNO₃, and the pH was measured with a digital pH meter.

The removal efficiency of Cd(II) and Zn(II) and the amount of metal ions adsorbed per specific amount of adsorbent at equilibrium (mg/g), q_e were calculated as:

$$\text{Removal efficiency (\%)} = 100 \times \frac{(C_0 - C_e)}{C_0} \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

Where q_e is the amount of metal adsorbed per specific amount of adsorbent (mg/g), C_0 and C_e are the initial and equilibrium solution concentrations (mg/L), respectively, V is the volume of solution (L), and m (g) is the weight of adsorbent.

Results

Characterization of nanocomposites

Figure 1 depicts the FTIR spectra of (a) PPy, (b) PPy-PVA, (c) PPy/Sb₂O₃, and (d) PPy-PVA/Sb₂O₃. The peaks seen at 1541, 1299, 1166, 1044, 895, and 789 cm⁻¹ are matched to stretching vibrations of the C=C, C-N, C-H in-plane deformation, C-H out-of-plane ring deformation, and N-H in-plane deformation, and C-H out-of-plane deformation (31). According to Figure 1, the intensity or wavenumber of the peaks of PPy varies slightly in the samples that were modified with PVA and Sb₂O₃. The reason for this event is the interaction between polypyrrole, surfactant, and additive and changes in bonding energies.

The crystalline nature of the composites appeared from XRD analysis. Figure 2 shows the XRD patterns of (a) PPy, (b) Sb₂O₃, and (c) PPy/Sb₂O₃. For pure polypyrrole, the main diffraction peaks were observed at $2\theta = 26.41^\circ$ and for Sb₂O₃, diffraction peaks were observed at $2\theta = 19.07^\circ$, $2\theta = 26.33^\circ$, $2\theta = 29.41^\circ$, and $2\theta = 49.83^\circ$. The XRD pattern of PPy/Sb₂O₃ reveals distinct crystalline peaks corresponding to the antimony oxide and polypyrrole, and this feature further supported the successful grafting of PPy onto the Sb₂O₃. The crystallinity of the composite is caused by the crystalline structure of Sb₂O₃.

Morphological characterization of composites was investigated using a scanning electron microscope. The SEM of polypyrrole composites is shown in Figure 3. Polypyrrole composites have a porous and spherical structure in aqueous media (32). Figure 3b shows the PPy-PVA nanocomposite. It is apparent from Figures 3a and 3b that the surface morphology of polypyrrole has

been considerably changed after the introduction of PVA into the polymeric matrix. Using surfactant decreases the tendency to form accumulations, because surfactant is prevented from aggregation of the particles, and the surface of PVA is covered with dispersed PPy Particles (33). As can be seen in images 3c and 3d, by adding Sb₂O₃, the size of the particles decreased and the uniformity of the particles increased. The reaction mixture is dispersed in particles, and therefore, all the Sb₂O₃ around the particles is covered with the polymer.

Effect of pH

According to the SEM micrographs of the composites, among the synthesized composites, PPy-PVA/Sb₂O₃ had the most uniform shape and special characteristics. Therefore, the removal experiments were performed using this adsorbent. One of the influential parameters in the adsorption process is the pH of the solution to control the amount of metal ions on the surface of the adsorbent.

The removal efficiency was investigated at different pH values ranging from 2 to 7 while other factors such as the concentration of metal ions, contact time, and temperature remained constant. At pH values higher than 7, removal experiments were not performed due to the formation of cadmium hydroxide and zinc hydroxide, which leads to a misinterpretation of the adsorption process.

Figure 4 shows the effect of solution pH on the removal of Cd(II) and Zn(II) ions using PPy-PVA/Sb₂O₃. The removal of Cd(II) and Zn(II) ions increased with increasing pH, and the maximum removal percentage of Cd(II) and Zn(II) ions occurred at pH 5 and 6, respectively. At lower pH values, protonation of the adsorbent surface may be possible (34). In addition, due to the high concentration of H⁺ ions, it may compete with the ions present in the active sites of the adsorbent, which reduces the adsorption of metal ions. When the pH increases, the competition between H⁺ ions and Cd²⁺ and Zn²⁺ ions in the active sites of the adsorbent decreases, which leads to the improvement of the adsorption process.

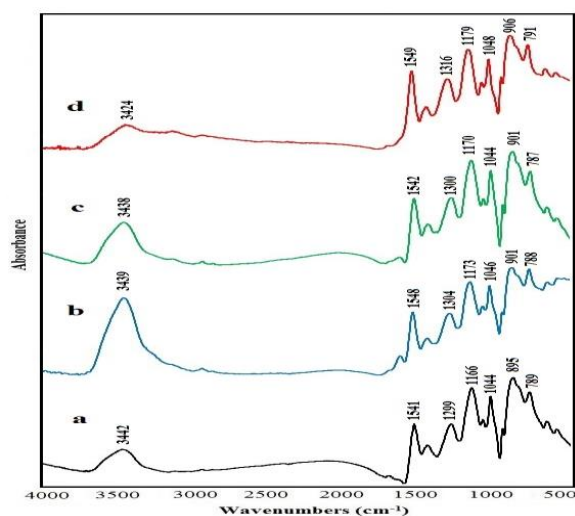


Figure 1. FTIR spectra of (a) pure PPy, (b) PPy-PVA, (c) PPy/Sb₂O₃, and (d) PPy-PVA/Sb₂O₃ nanocomposite

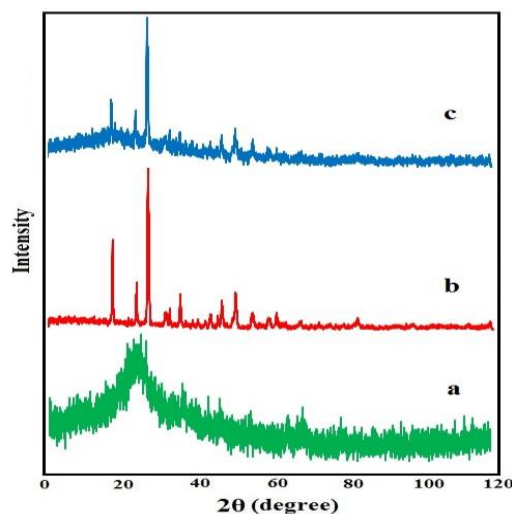


Figure 2. XRD patterns of (a) pure PPy, (b) Sb₂O₃, and (c) PPy/Sb₂O₃ nanocomposite

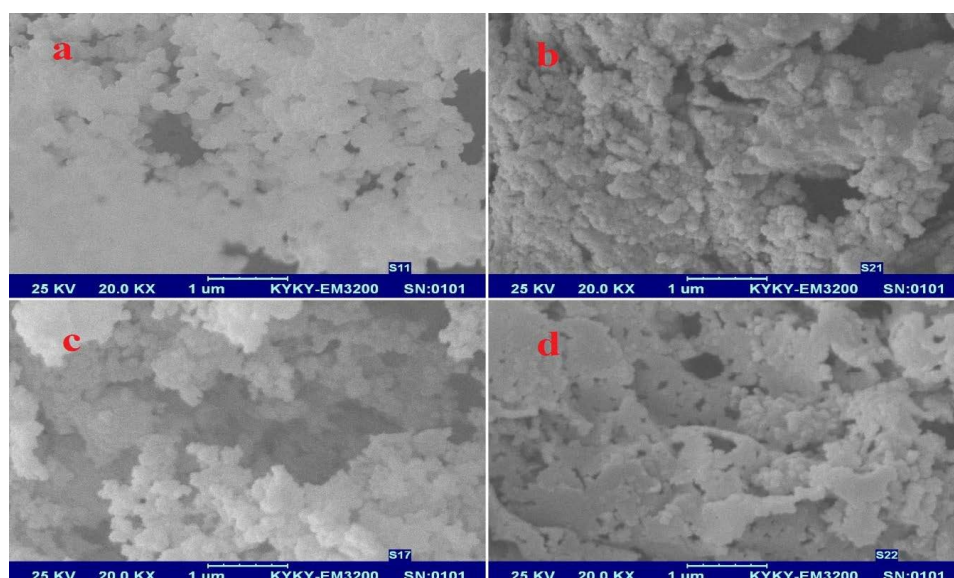


Figure 3. SEM images of (a) pure PPy, (b) PPy-PVA, (c) PPy-Sb₂O₃, and (d) PPy-PVA/Sb₂O₃ nanocomposite

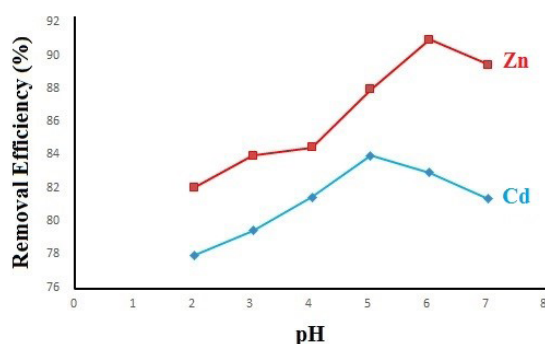


Figure 4. Effect of pH on the removal efficiency with PPy-PVA/Sb₂O₃ (Experimental conditions: Initial concentrations of heavy metal ions for Cd(II) and Zn(II), contact time, and amount of adsorbent were 50 mg/L, 45 min, and 0.3 g, respectively)

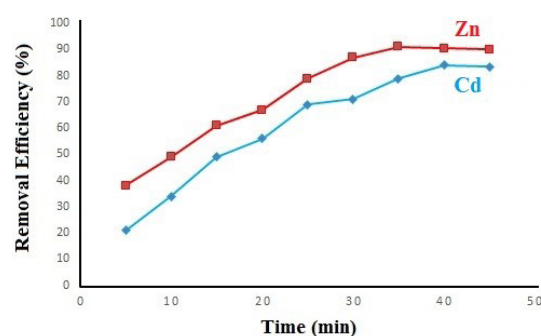


Figure 5. Effect of contact time on the removal efficiency with PPy-PVA/Sb₂O₃ (Experimental conditions: Initial concentrations of heavy metal ions for Cd(II) and Zn(II) and amount of adsorbent were 50 mg/L and 0.3 g, respectively)

Effect of contact time

The adsorption efficiency was measured by changing the contact time in the range of 5-45 minutes. The initial concentration of ions was 50 mg/L, and the adsorbent dosage was 0.3 g/30 mL of metal ion solution at the optimized pH (5 for Cd and 6 for Zn) was used. Figure 5 illustrates the uptake of Cd(II) and Zn(II) on PPy-PVA/Sb₂O₃. As seen, adsorption rates for the two metal ions are high at the beginning of the experiment. The initial rapid step may be related to the adsorption of metal ions on open adsorption sites of PPy-PVA/Sb₂O₃. As shown in Figure 5, the removal efficiency of the adsorbent reached the saturation limit after 40 minutes. Therefore, this time can be selected as the equilibration time for subsequent experiments.

Investigation on adsorption isotherm

Adsorption isotherm studies are based on the assumption that each adsorption site is equivalent and independent of the occupation or non-occupancy of adjacent sites. The adsorption isotherm was investigated using concentrations of 25, 50, 75, 100, 150, and 200 mg/L with an adsorbent amount of 0.3 g/30 mL. At constant temperature,

the equations describe the relationship between the equilibrium adsorption capacity (q_e) and the equilibrium concentration of metal ions in the solution (C_e), which is essential for modeling adsorption isotherms. To investigate the adsorption capacity of PPy-PVA/Sb₂O₃ for Cd(II) and Zn(II), Langmuir, Freundlich, and Temkin isotherms were used to analyze the experimental data (35). Langmuir (Eq. (3)), Freundlich (Eq. (4)), and Temkin (Eq. (5)) isothermal models could be expressed as given below:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (3)$$

$$\text{Log } q_e = \text{Log } K_f + \left(\frac{1}{n}\right) \text{Log } C_e \quad (4)$$

$$q_e = a + b \text{Ln } C_e \quad (5)$$

K_L is the Langmuir constant, q_e is the amount of metal adsorbed per specific amount of adsorbent (mg/g), C_e is the equilibrium concentration of the solution (mg/L), q_m is the maximum amount of desired metal ions to produce a monolayer (mg/g), K_f is the Freundlich adsorption isotherm constant (L/g), n is adsorption intensity, b_i is the heat of the adsorption (J/mol), and a_i is the equilibrium

binding constant.

The linear plots of adsorption isotherms using PPy-PVA/Sb₂O₃ nanocomposite for the Cd(II) and Zn(II) were shown in Figures 6 and 7, respectively. The Freundlich, Langmuir and Temkin adsorption constants calculated from the isotherms are presented in Table 1. According to R² values, it was visible the adsorption for Cd(II) and Zn(II) were well fitted with Langmuir model, indicating the adsorption was a monolayer chemisorption. The maximum theoretical adsorption capacity of PPy-PVA/Sb₂O₃ for Cd(II) and Zn(II) were calculated to be 17.33 and 15.361 mg/g, respectively. The values of *n* between 1 and 10 (1/*n* less than 1) indicate a suitable absorption (36).

As shown in Table 1, the values of *n* for the Freundlich model for both adsorption experiments were obtained greater than 1, indicating a strong interaction between the nanocomposites and Cd(II) and Zn(II). The high R² value of the Temkin isotherm also shows that the model matches the data.

Investigation of adsorption kinetics

Adsorption kinetics reveal important information about

the rate of adsorption and reaction progress pathways. To investigate the kinetic parameters, the pseudo-first-order kinetic model and the pseudo-second-order model were used. (37). The pseudo-first-order kinetic model can be shown as Eq. (6).

$$\text{Log}(q_e - q_t) = \text{Log } q_e - \left(\frac{K_1}{2.303} \right) t \quad (6)$$

In this equation, *t* is the contact time (min), *K₁* is the pseudo-first-order rate constant (1/min), *q_e* and *q_t* (mg/g) are the equilibrium adsorption capacity and adsorption at time *t*, respectively. The pseudo-second-order kinetic model can be shown as Eq. (7).

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

K₂ represents the pseudo-second-order rate constant (g/mg.min). The effect of the time parameter on the adsorption of Cd(II) and Zn(II) was investigated by adding 0.3 g of adsorbent to 30 mL of metal ion concentration solution of 50 mg/L with mixing times of 3, 5, 8, 10, 15, 20, 30, 40, 60, 80, 100, 120, 150, and 200 min at room temperature. The

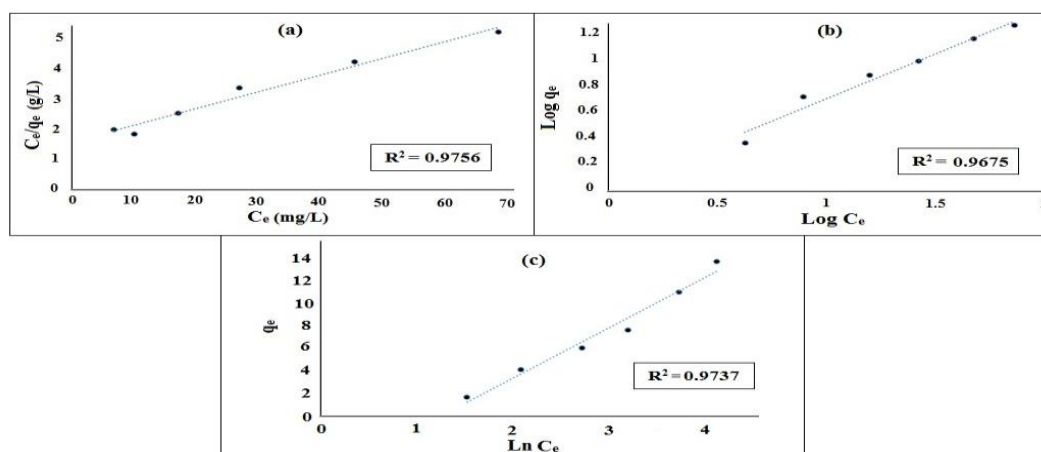


Figure 6. Langmuir (a), Freundlich (b) and Temkin (c) adsorption isotherms linear curve fitting of Cd(II) on PPy-PVA/Sb₂O₃ (Experimental conditions: initial concentrations of heavy metal ion for Cd(II) and amount of adsorbent were 25, 50, 75, 100, 150, 200 mg/L, and 0.3 g, respectively)

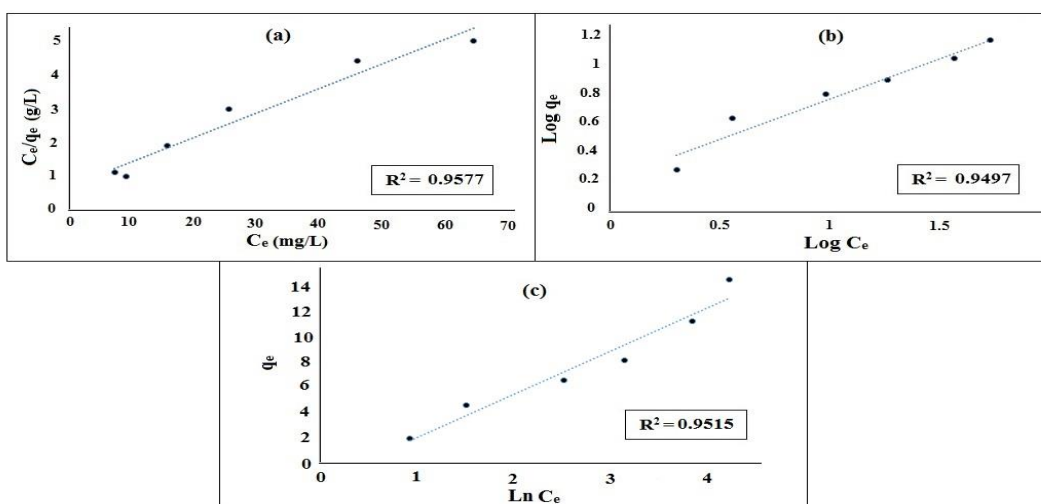
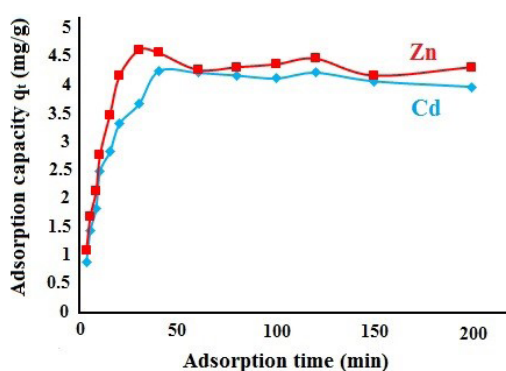


Figure 7. Initial Langmuir (a), Freundlich (b) and Temkin (c) adsorption isotherms linear curve fitting of Zn(II) on PPy-PVA/Sb₂O₃ (Experimental conditions: concentrations of heavy metal ion for Zn(II) and amount of adsorbent were 25, 50, 75, 100, 150, 200 mg/L, and 0.3 g, respectively)

Table 1. Langmuir, Freundlich and Temkin adsorption constants of Cd(II) and Zn(II) adsorption onto the PPy-PVA/Sb₂O₃ nanocomposites

Adsorption isotherm	constants	Cd(II)	Zn(II)
Langmuir	q_m (mg/g)	17.33	15.361
	K_L (L/mg)	0.032	0.061
	R^2	0.9756	0.9577
Freundlich	K_F (L/g)	1.034	1.78
	n	1.68	2.093
	R^2	0.9675	0.9497
Temkin	a_t	-3.4728	-0.6541
	b_t	3.5493	3.0106
	R^2	0.9737	0.9515

**Figure 8.** Effect of adsorption time on the adsorption capacity with PPy-PVA/Sb₂O₃

effect of the mixing time factor can be seen in Figure 8. The adsorbed amounts increase sharply and reach the equilibrium after 40 min. K_L , K_2 , and q_e are obtained from the slope and the intercept of the corresponding linear plots of $\text{Log}(q_e - q_t)$ versus t and t/q_t versus t . The calculation results are shown in Table 2. As could be expected, the correlation coefficients (R^2) of pseudo-second-order kinetics for Cd(II) and Zn(II) in PPy-PVA/Sb₂O₃ were found to be greater than those of the pseudo-first-order kinetic model in all experiments. Also, the q_e^{cal} values calculated by the pseudo-second-order model are very close to the q_e^{exp} values and confirm that the pseudo-second-order model is better in explaining the adsorption conditions.

Thermodynamic study

The solution temperature was changed (25, 35, and 50°C) on a stirrer, in a water bath, and with a thermometer during experiments to investigate the thermodynamic conditions of Cd(II) and Zn(II) ions adsorption on PPy-PVA/Sb₂O₃ nanocomposite. Thermodynamic parameters that include Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) are obtained from Eqs. (8) and (9):

$$\Delta G = -RT \ln K \quad (8)$$

$$\ln K = \frac{S}{R} - \frac{H}{RT} \quad (9)$$

In these equations, T (K) is the absolute temperature, R is the ideal gas constant (8.314 J/mol. K), and K is the

Table 2. Kinetic parameters of Cd(II) and Zn(II) adsorption onto the PPy-PVA/Sb₂O₃ nanocomposites

Kinetic models	Parameters	Cd(II)	Zn(II)
Pseudo-first-order	K_1 (1/min)	0.016	0.009
	R^2	0.3254	0.1926
Pseudo-second-order	K_2 (g/mg.min)	0.038	0.051
	q_e (mg/g)	4.238	4.442
	q_e , Experimental	4.237	4.651
	R^2	0.9947	0.9958

thermodynamic equilibrium constant (38). Also, K is equal to the ratio of q_e to c_e as Eq. (10):

$$K = \frac{q_e}{C_e} \quad (10)$$

The calculated values for ΔG , ΔH , and ΔS are shown in Table S1. At all temperatures, the negative values of ΔG indicate that the removal of Cd(II) and Zn(II) ions by PPy-PVA/Sb₂O₃ is a spontaneous process that increases with increasing temperature. ΔH values were also positive for all the studied experiments, which confirms the endothermic nature of the adsorption process and shows that the adsorption process is more active with increasing temperature. On the other hand, all the positive values of ΔS indicate that a random increase in the solid-liquid interface occurs during the adsorption of Cd(II) and Zn(II) ions on PPy-PVA/Sb₂O₃. The results obtained from the thermodynamics of the adsorption process, which show that heat increases the adsorption efficiency of metal ions, are consistent with the results of the adsorption isotherm and kinetic studies (38).

Investigating the effect of the concentration of metal ions on adsorption

The concentrations of 25, 50, 80, and 120 (mg/L) of Cd(II) and Zn(II) ions using composites at the optimum experimental conditions were investigated. The amount of adsorbent used was 0.3 g in 30 mL of solution. The results of the effects of Cd(II) and Zn(II) concentration on the removal percentage of nanocomposites are shown in Tables S2 and S3, respectively.

According to the data presented in the tables, the removal percentage increases with the increase in the concentration of metal ions for all composites, and the maximum amount of adsorption of the composites was obtained at a concentration of about 50 mg/L of metal ions. Increasing the number of metal ions in the solution increases the opportunity for the active groups on the adsorbent surface to bind to the metal ion, which leads to an increase in the removal efficiency. Then, with a further increase in the concentration of metal ions in the solution, the adsorption percentage decreased. At higher concentrations, the surfaces and internal cavities of the adsorbents are filled with metal ions, gradually saturated, and as a result, the concentration of metal ions remaining in the solution increases. It should be noted that the removal efficiency of the PPy-PVA composite for both metal ions

was better than that of pure PPy, indicating the efficient modification of PPy by PVA. Also, by looking closely at Tables S2 and S3, it can be seen that antimony oxide has a significant effect on the removal percentage. The particle size of the composites decreased with the addition of Sb_2O_3 . As a result, the contact surface of the adsorbent increases, which subsequently improves the removal percentage.

For a deeper understanding, Brunauer-Emmett-Teller (BET) measurements were performed on the surface of the composites. PPy-PVA/ Sb_2O_3 nanocomposite showed the highest surface area with $27.61 \text{ m}^2/\text{g}$ compared to pure PPy and PPy/ Sb_2O_3 composite, which were 6.27 and $15.63 \text{ m}^2/\text{g}$, respectively. As seen in the SEM image of PPy-PVA/ Sb_2O_3 , the increase in surface area is consistent with the decrease in particle size. Therefore, it can be concluded that increasing the surface area of PPy-PVA/ Sb_2O_3 increases the removal percentage.

Discussion

Adsorption mechanism

Two different mechanisms can be considered in the adsorption of heavy metal ions on PPy-PVA/ Sb_2O_3 : (I) physical adsorption on the surface of PPy-PVA/ Sb_2O_3 and (II) Chemisorption due to the reaction between PPy molecules with Cd(II) and Zn(II) ions. The synthesized composites based on polypyrrole have a spherical and porous structure with a high specific surface area. Therefore, metal ions can penetrate the adsorbent structure due to the porosity and holes and be adsorbed on the surfaces and gaps of the composites. Another adsorption mechanism that most likely occurs on the PPy/ Sb_2O_3 surface is through the electrostatic interaction of hydroxyl or chelation groups with N atoms located in the PPy structure and metal ions. It can be stated that the interaction between ions and the PPy matrix is the result of hybridization between the non-bonded pair of nitrogen atoms in the structure of polypyrrole and the empty orbital of metal ions such as Cd(II) (39,40). On the other hand, nitrogen species of PPy play a significant role in the process of reducing the polymer-metal interface.

Study of Desorption and Reusability

The recovery and reuse of an adsorbent is an important issue because it is related to the Current operating cost of the adsorption process. Desorption experiments were performed to regenerate the Cd(II) and Zn(II) loaded PPy-PVA/ Sb_2O_3 composite for adsorbent reuse. First, for the adsorption of Cd(II) and Zn(II), 0.1 g PPy-PVA/ Sb_2O_3 was contacted with 50 mL of 100 ppm Cd(II) and Zn(II) solution at pH 5 and 6, respectively. Desorption of Cd(II) and Zn(II) loaded PPy-PVA/ Sb_2O_3 adsorbent was done using 50 mL of 1 M NaOH solution. NaOH solution was used because it can reduce the electrostatic attraction force and also reduce the stability in the polypyrrole chain. The regenerated PPy-PVA/ Sb_2O_3 was investigated for six consecutive adsorption-desorption cycles to confirm the reusability of the adsorbent (Figure S1). The percentage of adsorption of the recycled adsorbent was 98.66% and

97.24% at the first cycle for Cd(II) and Zn(II), respectively. From the fifth cycle, the removal efficiency starts to decrease with a low gradient. This is due to incomplete desorption of metal ions. The test results show that the PPy-PVA/ Sb_2O_3 composite can be successfully reused for four consecutive adsorption-desorption cycles with the least possible decrease in its removal efficiency. Hence, the PPy-PVA/ Sb_2O_3 nanocomposite can be used as a high-performance and recyclable adsorbent for the adsorption of heavy metal ions.

Conclusion

In this study, the nanocomposites of polypyrrole (PPy/ Sb_2O_3) were synthesized in the presence of poly(vinyl alcohol) (PVA) to adsorb Cd(II) and Zn(II) ions from water. The synthesized composites were analyzed by Fourier transform-infrared (FTIR) spectroscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM). The results indicated that the Sb_2O_3 and PVA influenced the properties of synthesized nanocomposites. Adsorption experiments were carried out in a batch to remove heavy metal ions from aqueous solutions. The parameters affecting the adsorption process, including pH, contact time, and initial metal ion concentration, were investigated. The adsorption isotherms for Cd(II) and Zn(II) on PPy-PVA/ Sb_2O_3 were well fitted with the Langmuir model. The maximum theoretical adsorption capacities for Cd(II) and Zn(II) were calculated to be 17.33 and 15.361 mg/g , respectively. The kinetic results indicate that the pseudo-second-order kinetic model provides a better description of the adsorption process. Moreover, the thermodynamic parameters show the endothermic and spontaneous nature of the current adsorption process with an increase in PPy-PVA/ Sb_2O_3 . Based on these results, polypyrrole and its nanocomposites have potential for use as effective adsorbents due to their ease of synthesis, low cost, and regeneration efficiency for the removal of heavy metal ions from aqueous solutions.

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Authors' Contribution

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Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Ethical Approval

This study was conducted in compliance with ethical principles and guidelines, guaranteeing the right to human protection, safe handling of dangerous substances, and scientific integrity. Authors adhere to ethical standards in their research and reports to contribute to the advancement of knowledge.

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Supplementary Files

Supplementary file 1 contains Tables S1-S3 and Figure S1.

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