Surface modified polythiophene/Al$_2$O$_3$ and polyaniline/Al$_2$O$_3$ nanocomposites using poly(vinyl alcohol) for the removal of heavy metal ions from water: kinetics, thermodynamic and isotherm studies

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ABSTRACT

In this study, polythiophene/Al$_2$O$_3$ (PTh/Al$_2$O$_3$) and polyaniline/Al$_2$O$_3$ (PAn/Al$_2$O$_3$) nanocomposites in the presence of poly(vinyl alcohol) (PVA) as the surfactant were synthesized via in situ chemical oxidative polymerization method in aqueous medium. The synthesized nanocomposites were characterized by Scanning electron microscopy (SEM), Fourier transform-infrared (FTIR) spectroscopy and X-ray diffraction (XRD). Results indicated that the Al$_2$O$_3$ and poly(vinyl alcohol) influenced the properties of synthesized nanocomposites. The aim of this research was to investigate the sorption characteristic of polythiophene and polyaniline nanocomposites for the removal of heavy metal cations including Pb(II), Zn(II) and Cd(II) from aqueous solution. The factors that affected the adsorption equilibrium as well as the removal efficiency of the nanoadsorbents, i.e., contact time, metal ion concentration, pH and adsorption conditions were investigated in detail. From the kinetic results, it was concluded that the pseudo-second-order kinetic model was found to be the best at describing the adsorption process for Pb(II), Zn(II) and Cd(II) on PTh-PVA/Al$_2$O$_3$ and PAn-PVA/Al$_2$O$_3$. In addition, thermodynamic analysis suggests the endothermic and spontaneous nature of the present adsorption process with increased entropy on PTh-PVA/Al$_2$O$_3$ and PAn-PVA/Al$_2$O$_3$. The results suggest polythiophene, polyaniline and their nanocomposites have great potential to be used as efficient absorbent for the removal of heavy metal ions from water.

Key words: adsorption, kinetic, polyaniline, polythiophene, thermodynamic

HIGHLIGHTS

- Synthesize of polythiophene nanocomposites containing Al$_2$O$_3$.
- Products were investigated in terms of morphology.
- Batch adsorption experiment was performed for the removal of heavy metal ions.
- pH played vital role in the removal process.
- The factors that affected the adsorption equilibrium as well as the removal efficiency, i.e., contact time, metal ion concentration, pH and adsorption conditions were investigated.
INTRODUCTION

Heavy metal ions pollution and its effects on human life is one of the most studied environmental issues in recent years. Heavy metals are metallic chemical elements that have a relatively high density and are toxic or poisonous at low concentration (Zhou et al. 2018; Zhu et al. 2018). With the rapid development of industries such as metal plating, mining, batteries, fertilizers and paper industries, heavy metal ions are directly or indirectly discharged into rivers, lakes and ocean environments (Jaiswal & Pandey 2019). Toxic heavy metals ions such as arsenic, copper, zinc, nickel, cadmium, chromium, mercury and lead can be harmful to water and also remain a serious public health problem (Karthik & Meenakshi 2015; Yan et al. 2015; Seyf Hasankola et al. 2019). Aquatic organisms, such as fish, accumulate pollutants directly from contaminated water and indirectly via the food chain. Heavy metal toxicity as a result of fish consumption can result in damage or reduced mental and central nervous system function, lower energy levels, and damage to blood composition, lungs, kidneys, bones, liver and other vital organs. Long term exposure may result in slowly progressing physical, muscular, and Alzheimer’s disease, Parkinson’s disease, muscular dystrophy, and multiple sclerosis. Heavy metal toxicity is a chemically significant condition when it does occur. If unrecognized or inappropriately treated, toxicity can result in significant illness and reduced quality of life which can ultimately result in death (Piri et al. 2016; Isangedighi & David 2019).

Heavy metal ions in the trace amount are difficult to remove from the aqueous solution. Many techniques such as ion-exchange (Kamcev et al. 2018), physical and chemical precipitation (Chen et al. 2018a), membrane filtration (Rabbani Esfahani et al. 2019), electrochemical treatment (Barbosa et al. 2018), reverse osmosis (Rahimpour et al. 2018) and adsorption processes (Norouzian & Lakouraj 2015; Chen et al. 2018b) are extensively used methods for removing heavy metal ions from aqueous solutions. Each process has its advantages and disadvantages, but adsorption method is considered one of the most possible and effective techniques of...
producing the highest quality treated water (Yurekli 2019). Adsorption is a low-cost industrial separation technique, easy to operate and particularly effective when adsorbents with high adsorption capacity and selectivity are applied (Lidiya Mathew et al. 2019). In addition, it does not result in the formation of harmful substances (Jung et al. 2019).

Adsorption capacity of many adsorbents is still not high enough. Therefore, finding new materials for adsorbents with high adsorption performance and selectivity remains challenging (Tang et al. 2013; Abdi et al. 2017). Different types of absorbents have been proposed including active carbon (Ravulapalli & Kunta 2018), ferromagnetic materials (Liu et al. 2019), polymer (Mishra & Verma 2017) and biosorbents (Heraldy et al. 2018). Composite/nanocomposite materials are another group of adsorbents used mainly for the removal of heavy metal ions/dyes from wastewater/aqueous solutions. Composite/nanocomposite materials display better adsorption capacities, granulometric properties, chemical and thermal stabilities, reproducibilities, and also have better selectivities for the heavy metal ions/dyes removal compared to pure organic and inorganic materials (Sharma et al. 2015). Huang et al. introduced strong heavy metal ion sorbents based on copolymer microparticles with many functional groups including amino, imino and sulfonic groups synthesized by a chemical oxidative polymerization of m-phenylenediamine (mPDA) and p-sulfonic-mphenylenediamine (SPD) in pure water. The mPDA/SPD (95/5) copolymer microparticles demonstrated maximum yield, electrical conductivity, and Pb(II) and Cr(VI) (mainly as HCrO4-) adsorbability, but minimum Cu(II) adsorbability. However, the mPDA/SPD (50/50) copolymer microparticles demonstrated maximum Hg(II) adsorbability. It was also exhibited that the microparticles had good selective adsorptivity of up to 99.9% for Hg(II) and Pb(II) (Huang et al. 2012). Karthik et al. employed PANI grafted CS (PANIGCS) as an adsorbent for the removal of Pb(II) and Cd(II) ions from aqueous solution. It was reported that in the presence of other common metal ions, the adsorption of Pb(II) and Cd(II) ions onto the PANIGCS was negatively influenced and the maximum monolayer capacity was 16.07 and 14.33 mg/g for Pb(II) and Cd(II) ions, respectively. They showed that the sorption capacity of PANIGCS increased with the increase of pH, which was mainly due to both ion exchange and electrostatic attraction followed by complexation between the metal ions and PANIGCS (Karthik & Meenakshi 2015). Among the types of polymers with different structures and properties, the nitrogen or sulphur rich polymers have gained a great attention as an effective adsorbent for heavy metals due to the high ability and affinity of both nitrogen and sulphur atoms to bind with the metal ion (Wang et al. 2013; Nabi et al. 2014; Kharazi et al. 2018). Conducting polymers such as polyaniline (PAn), polypyrrole (PPy) and polythiophene (PTh) with interesting doping capabilities have been identified as candidates for adsorbents (Bhamik et al. 2016; Mishra et al. 2017; Xu et al. 2019). In order to obtain an adsorbent with high metal ion sorption efficiency, these polymers can be used combined with various materials, such as Chitosan/Sulphydryl functionalized graphene oxide (Li et al. 2015), multi-walled carbon nanotubes (Bhatia et al. 2019) and metal oxides (Eisazadeh et al. 2013; Lacuesta et al. 2018; Tanzili et al. 2018). Specifically, metal oxides have demonstrated a special adsorption affinity to some heavy metal ions, such as ferric oxides toward Pb(II) (Abdullah et al. 2016), manganic oxides possess to Cu(II) (Franzblau et al. 2016), Zn(II) on silicic oxides (Emadi et al. 2013), and many more (Mokadem et al. 2017; Bao et al. 2020). Therefore, the synthesis of conducting polymers with metal oxides has been extensively researched (Ghavami et al. 2014; Molaei et al. 2017).

In this work, conductive polymer nanocomposites such as polythiophene and polyaniline containing nanometer size Al2O3 were prepared via in situ chemical oxidative polymerization method in the presence of poly(vinyl alcohol) (PVA) as a surfactant. The structure and morphology were analyzed by XRD, SEM and FTIR. By using these nanocomposites as absorbent, the removal of heavy metal ions including Pb(II), Zn(II) and Cd(II) from water were investigated. The influences of various parameters such as contact time, initial concentration of heavy metal ions and pH on the sorption capacity were investigated. Also, based upon the experimental results, the adsorption kinetics, equilibrium and thermodynamics were discussed.

MATERIALS AND METHODS

Instrumentation

A pH meter model HANNA211, scanning electron microscope (SEM) model KYKY-EM3200, centrifuge model Z-36HK, Fourier transform infrared (FTIR) spectrometer thermo nicolet model Nexuf 670, X-ray diffraction (XRD) model Equinox 3000, magnetic mixer model MK20 (Germany), flame atomic absorption spectrophotometer model Thermo electron, digital scale model FR 200 and oven Binder model FD 23 were employed.
Materials

All reagents were used as received without further purification, unless stated otherwise. Materials used in this work were monomer of thiophene (d = 1.06 g/cm³), monomer of aniline (d = 1.02 g/cm³), ammonium peroxydisulfate (APS), sulfuric acid, hydrogen peroxide (H₂O₂), poly(vinyl alcohol) (PVA), ferric chloride (FeCl₃) and aluminum oxide (Al₂O₃) were obtained from Merck (Schuchardt, Germany). Thiophene monomer and aniline monomer were purified by simple distillation before using. Distilled water was employed throughout this work.

Nanocomposite preparation

Preparation of polythiophene/Al₂O₃ in the presence of PVA as the surfactant

The polythiophene was prepared chemically by using FeCl₃ as oxidant and H₂O₂ as co-oxidant in aqueous media. For the synthesis, 1 mL of thiophene monomer was individually added in 50 mL distilled water, and then 7.5 mL of H₂O₂ was added to solution. Then 0.02 g of FeCl₃, 0.2 g of PVA and 1.0 g of Al₂O₃ were dissolved in 50 mL distilled water, uniform solution was achieved using magnetic mixer for 30 min and dropwise added to monomer solution, which was maintained under constant stirring. The reaction was carried out for 5 h at room temperature. The product was centrifuged. In order 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 48 h. The schematic illustration of the synthesis process for PTh/Al₂O₃ composite in aqueous medium was depicted in Figure 1. As a reference sample, a pure PTh was prepared using the same method used previously, without Al₂O₃ and PVA (i.e., 100 mL distilled water containing 0.02 g FeCl₃, 7.5 mL H₂O₂, and 1 mL thiophene monomer).

Preparation of polyaniline/Al₂O₃ in the presence of PVA as the surfactant

For preparation of PAN-PVA/Al₂O₃ nanocomposite, 1.0 g ammonium peroxydisulfate (APS) was added to the aqueous solution of 100 mL sulfuric acid 1.0 M containing 1.0 g Al₂O₃ and 0.2 g PVA under stirring rate of 500 rpm. After 30 min, 1.0 mL fresh distilled aniline monomer was added to the stirred solution. The reaction was carried out for 5 h at room temperature. The product was centrifuged. In order 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 48 h. The Reaction scheme of the synthesis for PAN/Al₂O₃ composite was depicted in Figure 2. As a reference sample, pure PAN was prepared using the same method without Al₂O₃ and PVA (i.e., 100 mL sulfuric acid 1.0 M containing 1.0 g APS and 1.0 mL fresh distilled aniline monomer).

Batch adsorption experiment

The batch method was used to investigate the adsorption process of Pb(II), Zn(II) and Cd(II) on PTh-PVA/Al₂O₃ and PAn-PVA/Al₂O₃ nanocomposites. The standard heavy metal solutions used in the study were prepared from Pb(NO₃)₂, Zn(NO₃)₂ and CdCl₂, respectively with deionized water. All samples were shaken in 30 mL heavy
metal solution at an agitation speed of 400 rpm. The pH values of solution in these experiments were approximately 2–8. For determining the amount of metal ions removal by nanocomposites, metal ions solution (50 mg/L) was mixed with 0.3 g powder adsorbents and then stirred using magnetic mixer for 45 min. At the end of predetermined time intervals, the sorbate was filtered and the concentration of Pb(II), Zn(II) and Cd(II) were determined by atomic adsorption. All experiments were carried out twice to obtain average values. The deviation of this method was found to be less than 5%. The pH of the solution was adjusted using 0.1 mol/L NaOH and/or 0.1 mol/L HNO3 and the pH measurements were carried out in a digital pH meter. The removal efficiency of Pb(II), Zn(II) and Cd(II) and the amount of metal ions adsorbed per specific amount of adsorbent at equilibrium (mg/g), \( q_e \), were calculated as:

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]

where \( C_0 \) 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 AND DISCUSSION**

**Characterization of nanocomposites**

The chemical structure of obtained products was determined by FTIR spectroscopy. The FTIR spectroscopy of polythiophene and polyaniline nanocomposites were shown in Figures 3 and 4, respectively. The FTIR spectroscopy has provided valuable information regarding the formation of nanocomposites. Figure 3 shows the FTIR spectra of (a) pure PTh, (b) PTh-PVA, (c) PTh/Al2O3 and (d) PTh-PVA/Al2O3. It can be seen, pure PTh shows the presence of characteristic absorption bands at 601 cm\(^{-1}\) (C=S-C ring deformation stretching), 711 cm\(^{-1}\) (C-S bending), 1,042 cm\(^{-1}\) (C-H in-plane deformation), 1,217 cm\(^{-1}\) (C-H bending), 1,402 cm\(^{-1}\) (C=C symmetric stretching vibration of thiophene ring), 1,685 cm\(^{-1}\) (C=C asymmetric stretching), 2,923 cm\(^{-1}\) (C-H aliphatic stretching), 3,420 cm\(^{-1}\) (O-H stretching) (Prasad Bhattarai et al. 2019). According to Figure 3, the intensity or wavenumber of the peaks of pure PTh is slightly different in the samples which were modified with PVA and Al2O3. The reason of this phenomenon is the penetration of additives in the structure of polymers during the polymerization reaction and change in bonding energies.

Figure 4 shows the FTIR spectra of (a) pure PAn, (b) PAn-PVA, (c) PAn/Al2O3 and (d) PAn-PVA/Al2O3, respectively. The peaks of pure PAn are at 3,456 cm\(^{-1}\) (N-H amine, O-H hydroxyl), 2,924 cm\(^{-1}\) (C-H stretching vibration), 1,563 cm\(^{-1}\) (C=C stretching vibration of the quinoid ring), 1,468 cm\(^{-1}\) (stretching vibration of C=C of the benzenoid ring), 1,295 cm\(^{-1}\) (C-N stretching vibration), 1,120 cm\(^{-1}\) (C-H in-plane deformation) and 782 cm\(^{-1}\) (C-H out-of-plane deformation) (Dos et al. 2018). It can be seen in Figure 2(b)–2(d), existence of PVA and Al2O3 imposed the same effect as the one on pure polyaniline which results in the observed wavenumber shift and peak intensity change.

The crystalline nature of nanocomposites was determined from XRD analysis. The XRD patterns of polythiophene and polyaniline nanocomposites were shown in Figures 5 and 6, respectively. The XRD pattern of pure PTh (Figure 5(a)) shows a significant peak at \( 2\theta = 22.31^\circ \) which represents the semi-amorphous structure of polythiophene. The XRD pattern of Al2O3 was shown in Figure 5(b). The main peaks in Figure 5(b) are at \( 2\theta = 26.93^\circ \), \( 2\theta = 32.41^\circ \) and \( 2\theta = 49.13^\circ \). The mentioned peaks can be seen in XRD pattern of PTh-PVA/Al2O3 which confirmed the existence of Al2O3 nanoparticles in the polythiophene matrix. The crystallinity of the composite is caused by crystalline structure of Al2O3.

Figure 6 shows the XRD patterns of (a) pure PAn, (b) Al2O3 and (c) PAn-PVA/Al2O3. For polyaniline, diffraction peaks were observed at \( 2\theta = 19.75^\circ \) and \( 25.08^\circ \) and for Al2O3, diffraction peaks were observed at \( 2\theta = 26.93^\circ \), \( 2\theta = 32.41^\circ \) and \( 2\theta = 49.13^\circ \). The XRD pattern of PAn-PVA/Al2O3 shows distinct crystalline peaks corresponded to the aluminum oxide and PAn and this feature further supported the successful grafting of PAn on to the aluminum oxide. The crystallinity of PAn has been enhanced after grafting with aluminum oxide and this may be due to the intermolecular interaction between the aluminum oxide and PAn.

Morphological characterization of products was studied by using scanning electron microscope. The SEM micrographs of polythiophene and polyaniline nanocomposites were shown in Figures 7 and 8, respectively. It can be seen, it is apparent that PTh nanocomposites have spherical structure and PAn nanocomposites
have porous structure in aqueous media. Figures 7(b) and 8(b) show the PTh-PVA and PAn-PVA composites. The type of surfactant is known to influence the rate of polymer formation, particle size, size distribution, morphology, and homogeneity of particles (Kolodziejczyk et al. 2015). Using surfactant decreases the tendency to form agglomerates, because surfactant is prevented from gross aggregation of the particles and the surface of PVA is covered with uniformly dispersed PTh and PAn particles (Freitas et al. 2018). Figures 7(d) and 8(d) show the PTh-PVA/Al2O3 and PAn-PVA/Al2O3 nanocomposite, respectively. It can be seen in the micrographs, by adding Al2O3, the particle size decreased and the homogeneity of particles increased. The particles of Al2O3 not only coated on the surface of the particles but also in the inner parts. The reaction mixture diffuses into the particles and therefore all the Al2O3 inside and outside the particles are coated with the polymer. As a result, increasing the amount of additives in the reaction, such as Al2O3, influences the physical properties of product.

Effect of pH
According to the results of the products characterization, PTh-PVA/Al2O3 and PAn-PVA/Al2O3 had the most uniform particular shape and characteristics among the synthesized composites. Thus, the adsorption

Figure 3 | FTIR spectra of (a) pure PTh, (b) PTh-PVA, (c) PTh/Al2O3 and (d) PTh-PVA/Al2O3 nanocomposite.
experiments were carried out using these adsorbents. The pH values of the aqueous solution are an important controlling parameter in the adsorption process which affects the surface charge of adsorbent, the ionization of the functional groups onto the adsorbent surfaces and also the H\(^+\) ions concentration may react with the functional groups on the active sites on the adsorption surface.

To evaluate the effect of pH on the adsorption, the experiments were carried out at different pH ranging from 2 to 8 with an initial metal ions concentration of 50 mg/L. 0.3 g of adsorbent was added to 30 mL of metal ion solution and shaken for 45 min at room temperature. Finally, the sorbate was filtered using filter papers and finally concentration of heavy metal ions was determined. At pH values higher than 8, the experiments were not carried out due to the formation of lead hydroxide, zinc hydroxide and cadmium hydroxide which leads to incorrect interpretation of adsorption (Kurada & De 2018).

The results were shown in Figure 9 and the optimum pH values for Pb(II), Zn(II) and Cd(II) ions adsorption on PTh-PVA/Al\(_2\)O\(_3\) and PAn-PVA/Al\(_2\)O\(_3\) nanocomposites were listed in Table 1. At optimum pH, the nanocomposites acquired negatively charged surface which enhances the electrostatic attraction between the nanocomposites and metal ions followed by complexation. At high pH values, the negative charges are presents on the cell walls while at low pH values, the overall charge of the cells is positive due to protonation reactions which prevents the adsorption of positive ions.

Figure 4 | FTIR spectra of (a) pure PAN, (b) PAn-PVA, (c) PAn/Al\(_2\)O\(_3\) and (d) PAn-PVA/Al\(_2\)O\(_3\) nanocomposite.
Figure 5 | XRD patterns of (a) pure PTh, (b) Al₂O₃ and (c) PTh-PVA/Al₂O₃ nanocomposite.

Figure 6 | XRD patterns of (a) pure PAn, (b) Al₂O₃ and (c) PAn-PVA/Al₂O₃ nanocomposite.
Figure 7 | SEM images of (a) pure PTh, (b) PTh-PVA, (c) PTh/Al2O3 and (d) PTh-PVA/Al2O3 nanocomposite.

Figure 8 | SEM images of (a) pure PAN, (b) PAN-PVA, (c) PAN/Al2O3 and (d) PAN-PVA/Al2O3 nanocomposite.
For these cases, initial metal ions concentration of 50 mg/L and adsorbent dose of 0.3 g in 30 mL of metal ion solution at optimum pH (according to Table 1) were used. The results were shown in Figure 10 and the optimum equilibrium time for Pb(II), Zn(II) and Cd(II) ions adsorption on PTh-PVA/Al₂O₃ and PAn-PVA/Al₂O₃ nanocomposites were listed in Table 1. It can be seen in Figure 10, the adsorption rate for the three heavy metal cations are high at the start of the adsorption because the adsorption sites are open and metal ions interact easily with these sites. By increasing contact time, a larger amount of ions were removed and heavy metal ions uptake becomes almost constant after equilibrium time according to Table 1. Hence, these times can be chosen as equilibrium time for further experiments.

### Adsorption isotherms

The adsorption isotherm is based on the assumption that every adsorption site is equivalent and independent of whether or not adjacent sites are occupied. The adsorption isotherm for the removal of Pb(II), Zn(II) and Cd(II) ions was studied using concentration level of 50–200 mg/L at an adsorbent dosage of 300 mg/30 mL. This is important to note that the isotherms do not reflect any mechanisms of sorbate uptake; the equations show the relationship between metal concentration in solution and the amount of metal sorbed on a specific sorbent at a constant temperature. In order to investigate the adsorption capacities of PTh-PVA/Al₂O₃ and PAn-PVA/Al₂O₃ for Pb(II), Zn(II) and Cd(II), the most commonly used isotherm equations, namely Langmuir and Freundlich isotherms, were taken to analysis the experimental data (Tanzifi et al. 2017). Langmuir (Equation (3)) and Freundlich (Equation (4)) isothermal models could be expressed as given below.

\[
(C_e/q_e) = (1/q_mK_L) + (C_e/q_m)
\]

\[
\log q_e = \log K_F + (1/n) \log C_e
\]
where \( q_e \) is the amount of metal adsorbed per specific amount of adsorbent (mg/g), \( K_L \) is the Langmuir constants, \( C_e \) is the equilibrium concentration of the solution (mg/L), \( q_m \) is the maximum amount of metal ions required to form a monolayer (mg/g), \( K_F \) is the Freundlich adsorption isotherm constant (L/g) and \( n \) is adsorption intensity.

The linear plots of adsorption isotherm based on Langmuir and Freundlich model and the fitting parameters for the removal of metal ions using PTh-PVA/Al\(_2\)O\(_3\) were shown in Figure 11. Based on R\(^2\) values, it could be seen the adsorption for Pb(II) and Cd(II) were well fitted with Langmuir model and the adsorption for Zn(II) was well fitted with freundlich model. The maximum theoretical adsorption capacity of PTh-PVA/Al\(_2\)O\(_3\) for Pb(II), Zn(II) and Cd(II) were calculated to be 15.974, 19.841 and 18.248 mg/g, respectively. Figure 12 shows the linear plots of adsorption isotherm models and the fitting parameters for the removal of metal ions using PAN-PVA/Al\(_2\)O\(_3\) nanocomposite. It can be seen, the adsorption isotherms for Zn(II) and Cd(II) on PAN-PVA/Al\(_2\)O\(_3\) were well fitted with Freundlich model while for Pb(II) was well fitted with Langmuir model. The maximum theoretical adsorption capacity of PAN-PVA/Al\(_2\)O\(_3\) for Pb(II), Zn(II) and Cd(II) were calculated to be 15.698, 15.823 and 24.630 mg/g, respectively. The values of \( n \) between 1 and 10 (1/\( n \) less than 1) represent a favorable adsorption (Jeppu & Clement 2012). It can be seen in Figures 11 and 12, the \( n \) values for freundlich model was found to be greater than 1 for the all of the adsorption experiments, indicating a strong interaction between nanocomposites and Pb(II), Zn(II) and Cd(II).
### Figure 11
Langmuir and Freundlich adsorption isotherms linear curve fitting of Pb(II), Zn(II) and Cd(II) on PTh-PVA/Al₂O₃. (Experimental conditions: initial concentrations of heavy metal ions for Pb(II), Zn(II) and Cd(II) and amount of adsorbent were 50, 75, 100, 150, 200 mg/L and 0.3 g, respectively.)

|        | Langmuir model | Freundlich model |
|--------|----------------|-----------------|
| **Pb** | ![Graph](image1)  | ![Graph](image2) |
|        | \( q_e = 15.974 \text{ (mg/g)} \) | \( K_L = 0.237 \text{ (L/mg)} \) | \( K_r = 5.21 \text{ (L/(mg L)^n}) \) |
|        | \( R^2 = 0.9803 \) | | \( n = 3.645 \) |
| **Zn** | ![Graph](image3)  | ![Graph](image4) |
|        | \( q_e = 19.841 \text{ (mg/g)} \) | \( K_L = 0.05 \text{ (L/mg)} \) | \( K_r = 2.08 \text{ (L/(mg L)^n}) \) |
|        | \( R^2 = 0.9614 \) | | \( n = 2.014 \) |
| **Cd** | ![Graph](image5)  | ![Graph](image6) |
|        | \( q_e = 18.248 \text{ (mg/g)} \) | \( K_L = 0.165 \text{ (L/mg)} \) | \( K_r = 4.427 \text{ (L/(mg L)^n}) \) |
|        | \( R^2 = 0.9812 \) | | \( n = 2.794 \) |

### Figure 12
Langmuir and Freundlich adsorption isotherms linear curve fitting of Pb(II), Zn(II) and Cd(II) on PAn-PVA/Al₂O₃. (Experimental conditions: initial concentrations of heavy metal ions for Pb(II), Zn(II) and Cd(II) and amount of adsorbent were 50, 75, 100, 150, 200 mg/L and 0.3 g, respectively.)

|        | Langmuir model | Freundlich model |
|--------|----------------|-----------------|
| **Pb** | ![Graph](image7)  | ![Graph](image8) |
|        | \( q_e = 15.698 \text{ (mg/g)} \) | \( K_L = 0.063 \text{ (L/mg)} \) | \( K_r = 2.576 \text{ (L/(mg L)^n}) \) |
|        | \( R^2 = 0.9465 \) | | \( n = 2.613 \) |
| **Zn** | ![Graph](image9)  | ![Graph](image10) |
|        | \( q_e = 15.823 \text{ (mg/g)} \) | \( K_L = 0.044 \text{ (L/mg)} \) | \( K_r = 1.949 \text{ (L/(mg L)^n}) \) |
|        | \( R^2 = 0.8562 \) | | \( n = 2.314 \) |
| **Cd** | ![Graph](image11)  | ![Graph](image12) |
|        | \( q_e = 24.630 \text{ (mg/g)} \) | \( K_L = 0.016 \text{ (L/mg)} \) | \( K_r = 0.878 \text{ (L/(mg L)^n}) \) |
|        | \( R^2 = 0.6384 \) | | \( n = 1.548 \) |
Adsorption kinetics

The adsorption kinetics provides essential information about the solute uptake rate and the reaction pathways. In order to evaluate the kinetic parameters, two kinetic models, the pseudo-first-order kinetic model and pseudo-second-order kinetic model were applied (Tatry et al. 2019). The pseudo first-order kinetic model could be expressed as Equation (5).

\[ \log \left(\frac{q_e - q_t}{C_0}\right) = \log q_e - (K_1/2.303) t \]  

where \( K_1 \) is the pseudo first-order rate constant (1/min), \( t \) is the contact time (min), \( q_e \) and \( q_t \) (mg/g) are the equilibrium adsorption capacity and adsorption uptake at time \( t \), respectively. The pseudo-second-order kinetic model could be expressed as Equation (6).

\[ \frac{t}{q_t} = \frac{1}{(K_2 q_e^2)} + \frac{1}{q_e} \]  

where \( K_2 \) is the pseudo second-order rate constant (g/mg.min). The effect of mixing time on the removal of Pb(II), Zn(II) and Cd(II) was conducted by adding 0.3 g of adsorbent into 30 mL solution of 50 mg/L metal ion concentration with mixing times of 2, 5, 7, 10, 15, 20, 25, 30, 40, 50, 60, 120, 150 and 180 min at room temperature. \( K_1, K_2 \) and \( q_e \) could be determined from the slope and the intercept of the corresponding linear plots of \( \log \left(\frac{q_e - q_t}{C_0}\right) \) versus \( t \) and \( t/q_t \) versus \( t \), and the results were listed in Table 2. It can be seen, all correlation coefficients (R²) of the pseudo-second-order kinetics for Pb(II), Zn(II) and Cd(II) on PTh-PVA/Al₂O₃ and PAN-PVA/Al₂O₃ are higher than those of the pseudo-first-order kinetic model in all the studied experiments. In addition, the \( q_e^{cal} \) values obtained by pseudo-second-order model are closer to that of the \( q_e^{exp} \) values indicated that the pseudo-second-order model was better at describing the sorption system.

Thermodynamic study

The temperature of 50 mg/L heavy metal ions solution was changed (25, 35 and 45 °C) during adsorption experiments (for the optimum experimental conditions including pH and contact time) to study the thermodynamics of Pb(II), Zn(II) and Cd(II) ions adsorption on PTh-PVA/Al₂O₃ and PAN-PVA/Al₂O₃ nanocomposites. The thermodynamic parameters such as Gibbs free energy changes (ΔG), entropy change (ΔS) and enthalpy change (ΔH) were calculated from the following Equations (7) and (8):

\[ \Delta G = -RT \ln K \]  
\[ \ln K = (\Delta S/R) - (\Delta H/RT) \]  

where \( R \) is the ideal gas constant (8.314 J/mol.K), \( T \) (K) is the absolute temperature and \( K \) is the thermodynamic equilibrium constant (Shang et al. 2019). \( K \) is equal to the ratio of \( q_e \) to \( c_e \) as Equation (9):

\[ K = \frac{q_e}{c_e} \]  

| Table 2 | Kinetic parameters of Pb(II), Zn(II) and Cd(II) adsorption onto the PTh-PVA/Al₂O₃ and PAN-PVA/Al₂O₃ nanocomposites |
|-----------------|-----------------|-----------------|-----------------|
| **Type of adsorbent** | **Model** | **Parameters** | **Pb(II)** | **Zn(II)** | **Cd(II)** |
| PTh-PVA/Al₂O₃ | Pseudo-first-order | \( K_1 \) (1/min) | 0.013 | 0.0048 | 0.0156 |
| | | \( R^2 \) | 0.1303 | 0.0193 | 0.3076 |
| | Pseudo-second-order | \( K_2 \) (g/mg.min) | 0.045 | 0.131 | 0.109 |
| | | \( q_e \) (mg/g) | 4.955 | 4.417 | 4.794 |
| | | \( R^2 \) | 0.9951 | 0.9986 | 0.9994 |
| | | \( q_e \), Experimental | 4.865 | 4.475 | 4.8 |
| PAN-PVA/Al₂O₃ | Pseudo-first-order | \( K_1 \) (1/min) | 0.0168 | 0.0108 | 0.0214 |
| | | \( R^2 \) | 0.262 | 0.1326 | 0.4051 |
| | Pseudo-second-order | \( K_2 \) (g/mg.min) | 0.028 | 0.064 | 0.026 |
| | | \( q_e \) (mg/g) | 4.61 | 4.255 | 4.168 |
| | | \( R^2 \) | 0.992 | 0.9955 | 0.9951 |
| | | \( q_e \), Experimental | 4.485 | 4.24 | 3.975 |
The obtained values for \( \Delta G \), \( \Delta H \) and \( \Delta S \) were listed in Table 3. The negative values of \( \Delta G \) at different temperatures indicate the removal of Pb(II), Zn(II) and Cd(II) ions by PTh-PVA/Al\(_2\)O\(_3\) and PAn-PVA/Al\(_2\)O\(_3\) is a spontaneous process and the spontaneity increases with temperature. The positive values of \( \Delta H \) for all studied experiments confirmed the endothermic nature of the sorption process and points that the adsorption is more active at higher temperatures. In addition, the positive values of \( \Delta S \) reveal the possibility of increased randomness at the solid and liquid interface during the Pb(II), Zn(II) and Cd(II) ions sorption on PTh-PVA/Al\(_2\)O\(_3\) and PAn-PVA/Al\(_2\)O\(_3\). The results acquired from thermodynamic showing that heat promotes the adsorption of Pb(II), Zn(II) and Cd(II) ions on PTh-PVA/Al\(_2\)O\(_3\) and PAn-PVA/Al\(_2\)O\(_3\) composites are consisted with that obtained in the adsorption isotherm and adsorption kinetics investigations.

**Effect of initial concentration of metal ions on the adsorption**

The concentration of 50, 70, 100 and 150 (mg/L) of Pb(II), Zn(II) and Cd(II) ions from aqueous solution using nanocomposites at the optimum experimental conditions including pH and contact time were investigated. The amount of adsorbent was adjusted to 0.3 g into 30 mL solution. Tables 4–6 show the effect of initial concentration of Pb(II), Zn(II) and Cd(II) on the removal percentage of nanocomposites, respectively.

It can be seen, the removal percentage of Pb(II), Zn(II) and Cd(II) increases with the initial concentration of metal ions in regardless of PTh or PAn composites and the maximum value was obtained at about 70 mg/L. The increased number of the metal ions in the solution increases the opportunity of the active group to bind with the metal ion which increases the removal efficiency. Then by increasing the initial concentration of metal ions in the aqueous solution, the removal percentage was reduced. At high initial concentration, the absorbent surfaces become saturated with the ions and the residual metal ions concentration in the solution is increased.

### Table 3 | Thermodynamics parameters of Pb(II), Zn(II) and Cd(II) adsorption onto the PTh-PVA/Al\(_2\)O\(_3\) and PAn-PVA/Al\(_2\)O\(_3\) nanocomposites

| Type of adsorbent | Thermodynamic parameters | Pb(II) | Zn(II) | Cd(II) |
|-------------------|--------------------------|--------|--------|--------|
|                   | \( \Delta G \) (KJ/mol) T = 298 (K) | -5.895 | -2.289 | -4.764 |
|                   | \( \Delta G \) (KJ/mol) T = 308 (K) | -6.63  | -3.103 | -5.815 |
|                   | \( \Delta G \) (KJ/mol) T = 318 (K) | -7.387 | -4.08  | -6.977 |
|                   | \( \Delta H \) (KJ/mol) | 16.339 | 24.424 | 28.228 |
|                   | \( \Delta S \) (J/mol.K) | 74.6   | 89.5   | 110.7  |
| PTh-PVA/Al\(_2\)O\(_3\) | \( \Delta G \) (KJ/mol) T = 298 (K) | -2.405 | -1.285 | -0.324 |
|                   | \( \Delta G \) (KJ/mol) T = 308 (K) | -3.171 | -2.076 | -1.547 |
|                   | \( \Delta G \) (KJ/mol) T = 318 (K) | -3.999 | -3.058 | -3.204 |
|                   | \( \Delta H \) (KJ/mol) | 21.356 | 25.165 | 42.66  |
|                   | \( \Delta S \) (J/mol.K) | 79.7   | 88.6   | 144    |

### Table 4 | The effect of initial concentration of Pb(II) ion on the removal efficiency

| Type of adsorbent | Initial concentration: 50 (mg/L) | Initial concentration: 70 (mg/L) | Initial concentration: 100 (mg/L) | Initial concentration: 150 (mg/L) |
|-------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
|                   | Final conc. (mg/L) | Removal percentage (% w/w) | Final conc. (mg/L) | Removal percentage (% w/w) | Final conc. (mg/L) | Removal percentage (% w/w) | Final conc. (mg/L) | Removal percentage (% w/w) |
| PTh               | 5.38  | 89.24  | 4.47  | 93.61  | 11.39 | 88.61  | 34.6  | 76.93  |
| PTh-PVA           | 4.51  | 90.98  | 3.71  | 94.7   | 12.19 | 87.81  | 32.7  | 78.2   |
| PTh/Al\(_2\)O\(_3\) | 2.47  | 95.06  | 2.94  | 95.8   | 10.07 | 89.93  | 25.96 | 82.69  |
| PTh-PVA/Al\(_2\)O\(_3\) | 1.35  | 97.3   | 1.8   | 97.42  | 8.2   | 91.8   | 27.2  | 81.86  |
| PAn               | 6.67  | 86.66  | 11.22 | 83.97  | 25.16 | 74.84  | 52.09 | 65.27  |
| PAn-PVA           | 7.3   | 85.4   | 12.07 | 82.75  | 27.17 | 72.83  | 67.15 | 55.24  |
| PAn/Al\(_2\)O\(_3\) | 6.14  | 87.72  | 9.13  | 86.95  | 22.97 | 77.03  | 44.61 | 70.26  |
| PAn-PVA/Al\(_2\)O\(_3\) | 5.11  | 89.78  | 8.25  | 88.21  | 23.6  | 76.4   | 42.13 | 71.91  |
giving more attention to Tables 4–6, it is observed that aluminum oxide effectively influences the removal percentage. The particle size of composite was decreased by adding Al₂O₃. As a result, the total surface of adsorbent increased and also the removal percentage increased. It is noted that the removal efficiency of PTh-PVA and PAn-PVA for the heavy metal ions are more significant than that of pure PTh and pure PAn, indicating an efficient modification of PTh and PAn with PVA. Though, polyaniline nanocomposite possessed lower removal efficiency than polythiophene nanocomposite, it could be effectively used for the removal of heavy metal ions when they are present in lower concentration in water.

**Adsorption mechanism**

There are two different mechanisms in the adsorption of heavy metal cations on PTh-PVA/Al₂O₃ and PAn-PVA/Al₂O₃; (I) physical adsorption on the surface of PTh-PVA/Al₂O₃ and PAn-PVA/Al₂O₃ and (II) chemical adsorption through interactions of PTh and PAn molecules with Pb(II), Zn(II) and Cd(II) ions. PTh nanocomposites have spherical structure and PAn nanocomposites have a porous structure with high specific surface area. Therefore, metal ions can diffuse through the adsorbent porosity and adsorb on the surface of composites. Another probable adsorption mechanism occurring on the surface of PTh/Al₂O₃ is via electrostatic interaction of the hydroxyl groups or chelation with S atoms situating in the PTh matrix and metal ions such as Pb(II) ions (Figure 13(a)). Figure 13(b) presents a scheme mechanism for metal ions adsorption such as Cd(II) on PAn nanocomposite surface (Sun et al. 2017; Zhu et al. 2017). It can be anticipated that the interaction of Cd(II) and PAn

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**Table 5** | The effect of initial concentration of Zn(II) ion on the removal efficiency

| Type of adsorbent | Initial concentration: 50 (mg/L) | Final conc. (mg/L) | Removal percentage (%), w/w | Final conc. (mg/L) | Removal percentage (%), w/w | Final conc. (mg/L) | Removal percentage (%), w/w | Final conc. (mg/L) | Removal percentage (%), w/w |
|-------------------|---------------------------------|-------------------|----------------------------|-------------------|----------------------------|-------------------|----------------------------|-------------------|----------------------------|
| PTh               | 8.25                            | 83.5              | 13.14                      | 81.22             | 20.69                      | 79.31             | 41.17                      | 72.55             |
| PTh-PVA           | 9.13                            | 81.74             | 9.71                       | 86.12             | 21.55                      | 78.45             | 39.75                      | 73.5              |
| PTh/Al₂O₃         | 6.74                            | 86.52             | 10.04                      | 85.65             | 16.02                      | 83.98             | 31.12                      | 79.25             |
| PTh-PVA/Al₂O₃     | 5.3                             | 89.4              | 8.33                       | 88.1              | 17.7                       | 82.3              | 33.34                      | 77.7              |
| PAn               | 10.31                           | 79.38             | 23.21                      | 66.84             | 34.08                      | 65.92             | 73.23                      | 51.18             |
| PAn-PVA           | 8.11                            | 83.78             | 14.85                      | 78.81             | 31.19                      | 68.81             | 61.03                      | 59.31             |
| PAn/Al₂O₃         | 8.46                            | 85.08             | 9.71                       | 86.12             | 26.17                      | 73.83             | 53.85                      | 64.1              |
| PAn-PVA/Al₂O₃     | 7.55                            | 84.9              | 10.5                       | 85                | 27.6                       | 72.4              | 53.04                      | 64.64             |

**Table 6** | The effect of initial concentration of Cd(II) ion on the removal efficiency

| Type of adsorbent | Initial concentration: 50 (mg/L) | Final conc. (mg/L) | Removal percentage (%), w/w | Final conc. (mg/L) | Removal percentage (%), w/w | Final conc. (mg/L) | Removal percentage (%), w/w | Final conc. (mg/L) | Removal percentage (%), w/w |
|-------------------|---------------------------------|-------------------|----------------------------|-------------------|----------------------------|-------------------|----------------------------|-------------------|----------------------------|
| PTh               | 3.34                            | 95.32             | 5.27                       | 92.47             | 15.03                      | 84.97             | 34.17                      | 77.22             |
| PTh-PVA           | 4.92                            | 90.16             | 4.52                       | 93.54             | 23.93                      | 76.07             | 26.56                      | 82.29             |
| PTh/Al₂O₃         | 1.84                            | 96.32             | 2.33                       | 96.67             | 12.47                      | 87.53             | 29.04                      | 80.64             |
| PTh-PVA/Al₂O₃     | 2.1                             | 95.8              | 2.25                       | 96.78             | 9.2                        | 90.8              | 17.2                       | 88.53             |
| PAn               | 10.68                           | 78.64             | 25.4                       | 63.71             | 31.75                      | 68.25             | 62.65                      | 58.23             |
| PAn-PVA           | 14.8                            | 70.4              | 23.16                      | 66.91             | 34.27                      | 65.73             | 57.24                      | 61.81             |
| PAn/Al₂O₃         | 12.55                           | 74.9              | 17.05                      | 75.64             | 29.8                       | 70.2              | 50.88                      | 66.08             |
| PAn-PVA/Al₂O₃     | 10.4                            | 79.2              | 16.28                      | 76.74             | 31.3                       | 68.7              | 49.59                      | 66.94             |
matrix is a result of hybridizing between non-bonding pair of nitrogen atom of polyaniline and empty orbital of Cd(II) (Arabahmadi & Ghorbai 2017).

CONCLUSIONS

In summary, a serious of polymeric nanocomposites were prepared in the presence of poly(vinyl alcohol) (PVA) as the surfactant to be used for the adsorption of heavy metal ions from aqueous medium. The synthesized nano-composites were characterized by Scanning electron microscopy (SEM), Fourier transform-infrared (FTIR) spectroscopy and X-ray diffraction (XRD). Batch adsorption experiments were performed for heavy metal ions removal from aqueous solution. The equilibrium data were fitted to Langmuir and Freundlich isotherm models. From the kinetic results, it was concluded that the pseudo-second-order kinetic model was found to be the best at describing the adsorption process for Pb(II), Zn(II) and Cd(II) on nanocomposites. The thermodynamic parameters indicated the endothermic and spontaneous nature of the present adsorption process with increased entropy. The adsorption mechanism investigation suggested that the adsorption of Pb(II), Zn(II) and Cd(II) on composites may mainly through chemisorption such as chelation. On the basis of these results, PTh/Al2O3 and PAn/Al2O3 nanocomposites were found to be appropriate for the removal of heavy metal ions from the aqueous solution.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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