Tunning the Physical Properties of PVDF/PVC/Zinc Ferrite Nanocomposites Films for More Efficient Adsorption of Cd (II)

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Abstract
This work deals with the synthesis of ZnFe₂O₄ NPs and studies the effect of addition on the physical properties PVDF/PVC blend. XRD affirmed the formation of ZnFe₂O₄ NPs and HRTEM shows that the size of the prepared ZnFe₂O₄ NPs ranged from 20 to 55 nm. The effect of ZnFe₂O₄ on the behavior of PVDF/PVC was studied through XRD, ATR-FTIR, FESEM and UV–Visible spectroscopy. XRD revealed that the addition of ZnFe₂O₄ NPs enhanced the crystallinity of PVDF/PVC blend system and also confirmed the incorporation of ZnFe₂O₄ NPs by appearing a diffraction peak at 2θ equals 35°. ATR-FTIR affirmed the interaction between blend sample and ZnFe₂O₄ NPs by appearing new bands 554 cm⁻¹ and 421 cm⁻¹ which are corresponded to ZnFe₂O₄ NPs functional group with appearing a new band at 603 cm⁻¹. FESEM showed that the addition of ZnFe₂O₄ to PVDF/PVC blend improved surface properties, for example, roughness average has been increased from 319 to 414 nm while maximum height increased from 260 to 473 nm for PVDF/PVC and PVDF/PVC/10% ZnFe₂O₄, respectively. Optical properties and band gap calculations revealed that addition of ZnFe₂O₄ NPs changes the structure of polyblend samples which results due to the formation of localized states. The removal efficiency of Cd (II) by using PVDF/PVC/10% ZnFe₂O₄ reached about 50% at pH 6 after 60 min. The absorption mechanism as well as kinetics isotherm have been studied. It is found that adsorption of Cd (II) occurred through the Langmuir mechanism and fellow pseudo-second order isotherm.

Keywords PVDF/PVC · ZnFe₂O₄ NPs · Heavy metal removal of Cd (II)

1 Introduction
Because of the harmful effects of organic pollutants on human life and aquatic creatures, environmental remediation has become a prominent and rapidly growing subject of research [1]. The destruction of water supplies seems to be one of the most urgent environmental issues in the world. Water resources pollution is caused by heavy metals incorporation, such as cadmium, mercury, lead and chromium [2, 3]. Many researches are directed to remove pollutants from water like Etemadi et al. [4] produces polycarbonate/polyurethane/alumina membrane to eliminate humic acid molecules from wastewater, Zinatloo-Ajabshir et al. [8] uses a mixture from Sn- Ln metal oxides to remove pollutant from water, Rouhi et al. [9] prepare a nanocomposite from PPy/Fe₃O₄/halloysite nano clays/Ag/Co to remove methylene blue dye under visible sunlight, Taheri-Ledari et al. [10] uses Fe₂O₃/ZnO for degradation of methylene blue and Maleki et al. [11] synthesized magnetic geopolymer composed from bentonite clay and Fe₂O₄ for remove heavy metal ion from water. In the last decades, the whole world becomes very concerned with pollution of water by heavy metals. Because of its high toxicity and non-degradability dissimilar organic pollutants as they are biodegradable [12]. One of the most harmful heavy metal ions is Cd (II), which causes kidney failure and bone brittleness. In 1968, it was considered the first disease that occurred by pollution of the environment [13]. Recently, numerous techniques were used for the treatment and reuse...
of contaminated water by heavy metal ions involving, ion exchange [14], reverse osmosis [15], membrane filtration [16], chemical precipitation [17], Photocatalytic [18, 19] and adsorption [20]. Among all previous techniques, Adsorption is the most desirable technique due to its low cost, reproducibility, and effectiveness [21]. Adsorption of heavy metals is related to Adsorbent as well as adsorbate. For adsorbents, the uptake of heavy metals is affected by their concentration, PH, and contact time. Also, the adsorbate plays an important role in heavy metal removal. The removal of heavy metals can be done by the lattices which existed in spinel ferrite’s structure [22].

In recent years, there has been an increase in interest in the creation of nanostructures, due to their exceptional properties and potential uses in a variety of industries [23, 24]. Purity rate, shape, and grain size have all been shown to be effective variables in determining the properties and efficiency of nanocompounds. As a result, a vast number of studies have concentrated on designing nanocompounds while changing and managing the above parameters [25, 26].

Magnetic nanoparticles have nano size and remarkable magnetic characteristics, combining homogeneous and heterogeneous catalytic capabilities. Good activity, high reproducibility simple recycling, and repeatability are only a few of these characteristics. Because of their wide variety of applications, particularly in the fields of catalysis and nano-technology, these materials have received a lot of attention in recent years. The ferrite spinel, with the structural formula MFe$_2$O$_4$, is a key member of the magnetic nanomaterials family, which is used in a variety of applications [27–31]. ZnFe$_2$O$_4$ has attracted attention due to its magnetic behavior, chemical stability and larger surface area [32]. The chemical stability and removal efficiency of ZnFe$_2$O$_4$ can be enhanced by adding different types of polymers [33]. As, the polymer has chemical stability, good processability and flexibility [34]. As an important class of multidisciplinary materials, organic–inorganic hybrids, which have played major roles in a variety of applications [35]. Though, there are various types of polymers, poly (vinylidene fluoride) is considered one of the most desirable polymers because it has high flexibility, electroactive nature, and easy to prepare in film form with different sizes and shapes [36]. While PVC (poly vinyl chloride) is used because of its good mechanical, commercially available and easy processibility [3]. Meanwhile, the removal of Cd(II) from wastewater by using PVDF/PVC/ZnFe$_2$O$_4$ (x=0, 3, 7, 10 wt.%) nanocomposites films were not reported yet, thus, this work handed extreme emphasis on these nanocomposite films to eliminate Cd(II) from aqueous solution.

Herein, ZnFe$_2$O$_4$ nanosample was synthesized by flash method and combined with different concentrations to PVDF and PVC to form PVDF/PVC/x ZnFe$_2$O$_4$ (x = 3, 7, 10 wt.%) nanocomposites films to be used for heavy metal Cd(II) removal from wastewater. The batch experiment was studied under various parameters such as pH, contact time and the weight ratio of adsorbate, to determine the optimum conditions for maximum removal of Cd (II).

2 Materials and Methods

2.1 Materials

PVDF (Alfa Aesar 44,080), High-molecular-weight PVC (Fluka), Zinc nitrate [Zn(NO$_3$)$_2$.6H$_2$O], iron nitrate [Fe(NO$_3$)$_3$.9H$_2$O], Tetrahydrofuran solution (THF) and urea [CH$_3$N$_2$O] were purchased from LOBA, India.

2.2 Preparation of Zn-Ferrite

Nanosample ZnFe$_2$O$_4$ was synthesized by using the flash method. Firstly, Proper amounts (0.1 M) of iron nitrate were added to (0.1 M) of Zinc nitrates and mixed well with (0.7) urea. Secondly, the temperature of the mixture was raised to 250 °C till all fumes were ended. Lastly, the obtained powder was calcinated at 800 °C for 2 h with a rate 5 °C/min.

2.3 Preparation of PVDF/PVC/Zinc Ferrite Nanocomposites Films

In the beginning, PVDF and PVC powders were dried at 60 °C in a vacuum oven for around 2 h to remove any moisture content. After that, an equal quantity of PVDF and PVC was dissolved in Tetrahydrofuran solution (THF) separately until complete solubility, and then polymers were added to each other and stirred continuously until a homogenous solution was formed. To synthesis PVDF/PVC/x ZnFe$_2$O$_4$ films. Initially, Zinc ferrite NPs were added to the blend solution with weight percentage (3, 7, 10 wt. %). After that, the nanocomposite solution was sonicated by using a dip sonicator to prevent agglomeration of nanoparticles, at the last, the solution was transferred into a Petri dish and left in drier at 40 °C for around 6 h.

2.4 Measurement Techniques

XRD analysis of the produced samples was proceeded via PANalyticalX’Pert Pro target Cu-Kα with secondary monochromator Holland radiation with a tube running at 45 kV and wavelength = 0.1540 nm. A High-resolution transmission electron microscope (HRTEM) was applied by JEM-2100F electron microscope with 200 kV accelerating voltage. ATR-FTIR spectral was used in the range 4000–400 cm$^{-1}$ via spectrometer VERTEX 80 (Bruker Corporation, Germany). UV–Vis absorption spectra were performed from 200 to 1000 nm wavelength using Jasco UV–Vis (V-630) made in.

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Japan. FESEM was tested using Quanta 250 FEG worked at 20–30 kV. 3D micrographs as well as roughness parameters were obtained from FESEM images for each sample by using Gwyddion software.

2.5 Batch Experiment of Heavy Metal (Cd(II)) Removal

The experiment was carried out in 250 mL flasks with (0.1 g) of produced films in 2 ppm of metals nitrate to determine the appropriate pH values for heavy metal (Cd^{2+}) removal. The pH of the solution was changed from 2 to 8. The investigated solutions were thoroughly mixed for 1 h at room temperature using an electric shaker (ORBITAL SHAKER SO1) at 200 rpm. After that, the solutions were collected using a 0.2 m syringe filter. At 25 °C, atomic absorption spectroscopy (Zeenite 700P, Analytical Jena) was used to determine the heavy metal concentration. Every experiment was repeated three times, with the average results reported.

The optimum contact time was determined by repeating the previous process while keeping the pH at its optimal level and measuring atomic absorption after various contact times (1 to 24 h). The film removal efficiency is computed using the following formula [37].

\[
\text{Removal(adsorption)efficiency\%} = \frac{C_o - C_f}{C_o} \times 100\%
\]

where

- \(C_0\) : heavy metal soln at initial concentration (ppm)
- \(C_f\) : heavy metal soln at final concentration (ppm)

3 Results and Discussion

3.1 Structural Study

Figure 1 shows the XRD pattern of PVDF, PVC and PVDF/PVC/ZnFe_{2}O_{4} nanocomposite films. PVDF membrane shows two diffraction patterns at 2θ equals at 18.1° and 20.3° [38, 39]. Diffraction patterns of PVC indicated their amorphous character which has broad peaks at 2θ equals 16.6°, 18.4° and 24.3° [40]. For ZnFe_{2}O_{4} curve, the diffraction peaks of the as-prepared sample can be indexed to the cubic spinel Zn ferrite, according to the standard PDF card (No.79-1150). It has diffraction peaks at 2θ equals 29.7°, 35.0°, 56.3° and 62.1° which corresponded to (220), (311), (511) and (440) lattice plane, respectively [41].

The Debye–Scherrer equation was used to calculate the average crystallite size (S) of ZnFe_{2}O_{4} across the (311) crystal plane [42].

Fig. 1 XRD Pattern of the prepared samples
\[ S = \frac{0.9 \lambda}{\beta \cos \theta} \]  

where the X-ray wavelength is \( \lambda \) (0.154 nm), \( \beta \) is the full-width at half-maximum and \( \theta \) is the diffraction angle. It is seen that ZnFe\(_2\)O\(_4\) has an average crystal size equal to 30 nm.

For PVDF/PVC film displays a broad and weak diffraction peak, relating to the amorphous feature of polymers. By increasing the weight ratio of ZnFe\(_2\)O\(_4\) from 3 to 10%, the crystallinity gets better and diffractions peaks become clearer compared to 0% weight ratio of ZnFe\(_2\)O\(_4\). Also, there is a diffraction peak that appeared at 2\( \theta \) equal 35.0° and it is intensity increased with increasing ZnFe\(_2\)O\(_4\) NPs affirmed the formation of ZnFe\(_2\)O\(_4\) NPs in the PVDF/PVC matrix. So, the addition of ZnFe\(_2\)O\(_4\) NPs at different weight percentages has a significant role in the crystallinity enhancement of polymers.

Figure 2 represents the HRTEM, SAED and size distribution of ZnFe\(_2\)O\(_4\) NPs, it has irregular shapes between semi-spherical and deformed cubic. Selected area electron diffraction (SAED) patterns of the samples were revealed, confirming the polycrystalline nature of pure ZnFe\(_2\)O\(_4\) NPs with high crystallinity. The average particle size of ZnFe\(_2\)O\(_4\) NPs is ranged from 20 to 55 nm.

Figure 3 displays FTIR spectra of PVDF, PVC and PVDF/PVC/x ZnFe\(_2\)O\(_4\); x = 0%, 3%, 7% and 10% films. PVDF has a characteristic band at 1400 cm\(^{-1}\) in the FTIR spectra of pure PVDF (Fig. 2a) belongs to the CH\(_2\) wagging mode associated PVDF chain [43]. The asymmetric and symmetric stretching vibrations of CF\(_2\) were ascribed to the bands that occurred at 1179 cm\(^{-1}\) and 1061 cm\(^{-1}\),
respectively. The out of plane C–H bending is shown by the band at 973 cm\(^{-1}\) [44]. Asymmetrical stretching vibrations of C–C–C and C–F stretching vibrations were attributed to the bands at 870 cm\(^{-1}\) and 842 cm\(^{-1}\), respectively [45]. CF\(_2\) bending vibration was ascribed to the bands that emerged at 614 cm\(^{-1}\) and 489 cm\(^{-1}\) [46]. For PVC, the asymmetric stretching vibration of the C–H band is seen at 2913 cm\(^{-1}\). At 1422 cm\(^{-1}\), the stretching vibration of the C–H band can be noticed. CH\(_2\) deformation and the rocking mode of the C–H bond near Cl are attributed to bands at 1334 cm\(^{-1}\) and 1245 cm\(^{-1}\), respectively. At 1098 cm\(^{-1}\), the C–C stretching vibration is detected. Trans–CH and cis–CH wagging modes may be seen at 958 cm\(^{-1}\) and 614 cm\(^{-1}\), respectively. C–Cl has a stretching vibration of 827 cm\(^{-1}\) [47–50].

For PVDF/PVC blend spectra, it combined the characteristic feature of both polymers with changing of the intensity of them which affirmed that there is a reaction between PVDF and PVC. For PVDF/PVC films doped with different weight ratios of ZnFe\(_2\)O\(_4\)NPs (3%, 7% and 10%). There are new bands 554 cm\(^{-1}\) and 421 cm\(^{-1}\) which are corresponded to Zn–O bonds intrinsic stretching vibration of tetrahedral sites and Fe–O bonds in octahedral sites, respectively [51]. Also, there is new band appeared with an increasing ZnFe\(_2\)O\(_4\)NPs ratio at 603 cm\(^{-1}\) and the intensities of bands decreased by increasing ZnFe\(_2\)O\(_4\) content. The IR intensity variation can be an indication of the interaction between parts in prepared films.

Figure 4 was representative of FESEM images of prepared films. The image of surface showed that ZnFe\(_2\)O\(_4\) nanofiller were spread homogeneously in PVDF/PVC matrices which has utilities in different applications. By increasing weight % content of ZnFe\(_2\)O\(_4\) nano powder, the surfaces of the blend seem to be more roughness. Pure PVDF/PVC image shows a smooth surface with high porosity.

Figure 5 displays the surface roughness of PVDF/PVC films which are doping with a different weight percentages of ZnFe\(_2\)O\(_4\) nanopowder. As it obtained from Table 1 all roughness parameters increased with increasing filler content. For example, the average has been increased from 319 to 414 nm while the maximum height increased from 260 to 473 nm for PVDF/PVC and PVDF/PVC/10% ZnFe\(_2\)O\(_4\), respectively. Physical adhesion for prepared films is strongly affected by these parameters (roughness average and height). As roughness height act as hooks and facilitate the connection between films and surrounding [52]. The change in roughness parameter may be related to filler in polymeric matrices. Consequently, we can control the roughness parameters through additives in the blend according to the desired applications.

### 3.2 Optical Properties

The UV–visible spectrum is an essential measurement to calculate the energy gap of amorphous and crystalline materials. The basic absorption is related to the excitation of electron from the top of the valance band to the bottom of the conduction band, it also can be used for determining the value and nature of the band gap. Figure 6 which
shows UV–Visible absorbance spectra of PVDF/PVC/x ZnFe$_2$O$_4$; x = 0%, 3%, 7% and 10% nanocomposite films. For PVDF/PVC blend, there are two peaks at 205 nm and 279 nm which corresponded to n → π* and π → π* transitions which corresponded to a chromophoric group of PVDF and PVC polymer blend [53, 54]. As seen in for PVDF/PVC doped with a different weight percentage of ZnFe$_2$O$_4$ NPs, the peaks at 205 nm shift toward a higher wavelength (red shift). This means that there is complexation between PVDF/PVC and ZnFe$_2$O$_4$ NPs.

The absorption edge defines the excitation of an electron by an incident photon from lower energy to a higher energy state, which may be calculated by extrapolating the linear part of the absorption coefficient (α) with photon energy (hν). The absorption coefficient is calculated using the following equation, where A and d are the absorbance and thickness of the prepared sample [47].

$$\alpha = \frac{2.303A}{d}$$  \hspace{1cm} (3)

As observed in Fig. 7, when compared to the PVDF/PVC blend sample, the values of the absorption edge are reduced as seen in Table 2. This is due to the formation of localized states within the band gap, as well as the changing number of final states in the system.

An optical absorption spectrum is a useful tool for calculating the optical band-gap energy of any material. The optical band gap’s nature and value are checked using critical absorption, which corresponds to the electron’s excitation from the valence band to the conduction band. The strong-absorption area can be studied using Tauc’s equation, which is provided below [55].

Fig. 4 FESEM micrographs of PVDF/PVC/xZnFe$_2$O$_4$ films; a x = 0%, b 3%, c 7% and d 10%
Fig. 5 3D micrographs of PVDF/PVC/xZnFe₂O₄ films; a x = 0%, b 3%, c 7% and d 10%

Table 1 Roughness parameters (roughness average Ra, root mean square roughness Rq, Maximum height of roughness Rp) of PVDF/PVC/x ZnFe₂O₄ films; x = 0%, 3%, 7% and 10%

| Sample | Ra (nm) | Rq (nm) | Rp (nm) |
|--------|---------|---------|---------|
| X = 0  | 319     | 45      | 260     |
| X = 3% | 340     | 59      | 315     |
| X = 7% | 403     | 100     | 440     |
| X = 10%| 414     | 113     | 473     |

Fig. 6 UV–Vis spectra of the prepared samples

Fig. 7 Absorption coefficient- photon energy relation of the prepared samples

Table 2 Absorption edge, direct and indirect transitions energy band gap values of PVDF/PVC/x ZnFe₂O₄ films; x = 0%, 3%, 7% and 10%

| Sample  | Absorption edge (eV) | Direct band gap (eV) | Indirect band gap (eV) |
|---------|----------------------|----------------------|------------------------|
| X = 0   | 4.8                  | 5.0                  | 3.7                    |
| X = 3%  | 4.6                  | 4.9                  | 3.6                    |
| X = 7%  | 4.5                  | 4.8                  | 3.3                    |
| X = 10% | 4.4                  | 4.8                  | 2.9                    |
where \( \alpha_o \) is constant. The variation of \((\alpha h \nu)\) \(^2\) and the \((\alpha h \nu)\) \(^{1/2}\) intercepting with the photon energy axis is depicted in Fig. 8. Fitting the linear part of the curve and determining the intersection of the straight line with the \( h \nu \) axis yields the energy gap. As seen in Table 2, compared to PVDF/PVC, the direct and indirect band gap energy values of PVDF/PVC/x\% ZnFe\(_2\)O\(_4\) decrease. This result revealed that the structure of the blend sample had changed, resulting in the formation of a localized state.

\[
(\alpha h \nu)^2 = \alpha_o (h \nu - E_g) \quad \text{for allowed direct transition}
\]

\[
(\alpha h \nu)^{1/2} = \alpha_o (h \nu - E_g) \quad \text{for allowed indirect transition}
\]

3.3 Batch Experiment

The Cd (II) uptake behavior by using PVDF/PVC/x\% ZnFe\(_2\)O\(_4\) nanocomposite films was studied at various pH and contact time as experimental factors to find the best conditions for heavy metal removal. Figure 9 displays the pH solution effect on adsorption performance. It is shown that all prepared films have the same trend which is increasing pH is accompanied by the increasing value of the adsorption of Cd (II) ion. At low pH, adsorption of Cd (II) has low values (from 3 to 10) % may be it is due to a large amount of H\(^+\) which compete Cd\(^{2+}\) over the adsorbent’s active sites [56]. By increasing value up to 6, consequently, the number of H\(^+\) decreasing and for Cd (II) adsorption, additional active sites become supplied [57] the removal efficiency % reached to about 30% for PVDF/PVC/10\% ZnFe\(_2\)O\(_4\). OH\(^-\) ions are present in solution at a basic pH (i.e. 8) causing the formation of Cd (OH)\(_2\) [58]. So, the up takings of Cd (II) ions were due to adsorption and precipitation. The maximum adsorption was observed for PVDF/PVC/10\% ZnFe\(_2\)O\(_4\) as between all prepared samples this one has maximum roughness as well as maximum roughness height as mentioned above. Finally, we may infer that pH 6 is the best choice for the removal of Cd (II).

The contact time is another factor that has a significant impact on heavy metal ion adsorption. Figure 10 explains the relationship between adsorption of Cd (II) ions by using PVDF/PVC/x\% ZnFe\(_2\)O\(_4\); x = 0, 3, 7 and 10\% nanocomposite films and the contact time over range (10–60) min. It is clear, as contact time is increased, the adsorption of Cd (II) ion on the surface of prepared samples also is increased. In the beginning, there were many active sites available as a result the adsorption increased by increasing contact time till the equilibrium state is reached. PVDF/PVC/10\% ZnFe\(_2\)O\(_4\) has the highest removal efficiency, reaching nearly...
50% after 60 min, which could be due to the number of active sites on its surface [59]. On the other hand, it is clearly observed that the composition of films plays an important role in adsorption efficiency. As the weight percentage of ZnFe₂O₄ in PVDF/PVC blend increased the removal efficiency increased too. This may be related to the surface properties such as roughness average and maximum height which act as trapping sites to capture the heavy metal. So, PVDF/PVC/10% ZnFe₂O₄ has the highest roughness average and maximum average height consequently it has maximum removal efficiency.

Finally, employing a PVDF/PVC/10% ZnFe₂O₄ nanocomposite film, the best conditions for Cd (II) adsorption are pH 6 for 60 min.

The only way for knowing the adsorption mechanisms which were occurred in the adsorption process is done through studying adsorption isotherm and kinetics [62]. Langmuir and Freundlich isotherms are the two isotherms that are used to describe adsorption. Equations (6) and (7) were used to represent the Langmuir and Freundlich isotherms, respectively.

\[
\frac{C_e}{q_e} = \frac{1}{k_d q_m} + \frac{C_e}{q_m}
\]

(6)

\[
\ln q_e = \ln k_f + \frac{1}{n} \ln C_e
\]

(7)

where \(q_e\) and \(q_m\) (mg g\(^{-1}\)) denote the equilibrium and maximum adsorption capacities, respectively, and \(K_f\) (L mg\(^{-1}\)) denotes the affinity binding constant, and \(K_f\) and \(n\) (physical constants) denote the adsorption capacity and intensity of adsorption, respectively.

The Langmuir isotherm describes monolayer adsorption at the sites which are equivalent and homogeneous with similar adsorption energies, while the Freundlich isotherm describes heterogeneous surfaces [63]. We discovered that all samples matched the Langmuir model behavior by fitting Fig. 11. On the other hand, fitting Fig. 12 revealed that none of the samples followed the Freundlich isotherm. As a result, Cd (II) adsorption on the produced sample’s surface occurred via monolayer adsorption (Fig. 13).

Heavy metal adsorption kinetics was primarily explored using pseudo first order or pseudo second order kinetics. The physisorption is explained by pseudo first order kinetics. A Physisorption is a weak form of adhesion that relies on vanderwaals forces rather than chemical bonds. As a result, this type of adsorption can be reversed. However, pseudo-second order kinetics is associated with chemisorption adsorption, which occurs as a result of two processes. It is the first reaction, and it soon extends equilibrium. The second, on the other hand, leaks slowly and takes a long time to attain equilibrium [59]. By employing electron sharing, bonds are formed between adsorbents and adsorbates in chemisorption. As a result, it is more difficult than physisorption. The intra particle diffusion kinetic model is also one of the kinetic models. This model was studied by Weber and Morris model is studying. They discovered that the intra particle diffusion model is the single rate-determining stage, and adsorbate removal is carried out in a quick process [64].

Three models were used to investigate the kinetics of the adsorption mechanism:

**Pseudo first-order model:**

\[
\ln (q_e - q_t) = \ln q_e - \frac{k_1}{2.303} t
\]

(8)

**Pseudo second-order model:**

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

(9)

**Inter particle diffusion model:**

\[
q_t = k_3 t^{1/2} + C
\]

(10)

where \(k_1\), \(k_2\), and \(k_3\) are the pseudo first, second order and inter particle diffusion rate constants in (min\(^{-1}\)) and (g mg\(^{-1}\) min\(^{-1}\)), respectively.

Further, the majority of heavy metal ions adsorption on the surface of produced samples nanocomposites films fit well with the pseudo-second order kinetic model, refereeing to the Fig. 14 compared to that for pseudo-first order Fig. 13 and inter particle diffusion model Fig. 15. So, the adsorption of Cd (II) by using PVDF/PVC/x wt% ZnFe₂O₄; x = 0, 3, 7 and 10 nanocomposites films was done through Langmuir isotherm and the adsorption mechanism kinetics is pseudo second- order model. It can be seen that Table 3 represents the comparative study between previous works.
and the present work and seen that PVDF/PVC/10 wt % ZnFe₂O₄ are the best for removing Cd (II).

4 Conclusion

ZnFe₂O₄ nano filler with different weight percentages was synthesized successfully by using flash method. These nanofillers were added to PVDF/PVC blend to form nanocomposite films of formula PVDF/PVC/x% ZnFe₂O₄; x = 0, 3, 7 and 10. The structure of obtained samples was studied through XRD and ATR-FTIR and confirmed the changes in structure and complexation between blend sample and ZnFe₂O₄ NPs. The morphology and surface of samples were observed by using FESEM, it is observed that by increasing the weight percentage the roughness average has been increased from 319 to 414 nm while maximum height increased from 260 to 473 nm for PVDF/PVC and PVDF/PVC/10% ZnFe₂O₄, respectively. The absorption edge and band gap energy are decreased compared to blend sample as it is decreased from 4.8 eV for PVDF/PVC/0% ZnFe₂O₄ to 4.4 eV for PVDF/PVC/10% ZnFe₂O₄. Also, the band energy gap for direct and indirect transition show decrease in their energies by increasing Zn-ferrite content. In addition to, the nanofiller enhanced the removal efficiency for Cd (II) from the wastewater which was reached to 50% at pH 6 for 60 min by using PVDF/PVC/10% ZnFe₂O₄. The adsorption process occurred through the Langmuir mechanism and fellow pseudo-second order isotherm. Finally, we concluded that the sample with composition PVDF/PVC/10% ZnFe₂O₄ has the optimum physical properties and highest removal efficiency for Cd (II).
Fig. 12 Freundlich isotherms for the prepared nanocomposite films
Fig. 13  Pseudo-first-order model for the prepared nanocomposite films
Fig. 14 Pseudo-second-order model for the adsorption of Cd(II) for the prepared nanocomposite films
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