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In Situ Polyaniline Immobilized ZnO Nanorods for Efficient Adsorptive Detoxification of Cr (VI) from Aquatic System

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Abstract: The elimination of toxic heavy metal ions from wastewater has been found to be of great importance in human as well marine animal wellbeing. Among various heavy metals, Cr (VI) has been found to be one of the highly toxic and carcinogenic heavy metals which are found to be dissolved in the water stream, the urgent treatment of which needs to be a priority. The present study demonstrates the fabrication of zinc oxide nanorods (ZnO NRs) and an immobilized polyaniline nanorod (ZnO@PAni NR) composite through an in situ free radical polymerization reactions. The material synthesis and purity were verified by X-ray diffractometer (XRD), Fourier transform infrared (FTIR), scanning electron microscope (SEM), energy dispersive spectroscope (EDS), and transmission electron microscope (TEM). Further, ZnO@PAni NRs were applied as an adsorbent for Cr (VI) in the aquatic system and exhibited a tremendous removal efficiency of 98.76%. The impact of operating parameters such as dose effect and pH on adsorption properties were studied. The uptake mechanism of Cr (VI) by ZnO@PAni was best explained by pseudo-second-order reaction, which suggested that the adsorption of Cr (VI) by the synthesized adsorbent material was processed by chemisorption, i.e., through formation of chemical bonds. The adsorption process proved viable and endothermic thermodynamically, and best supported by a Langmuir model, suggesting a monolayer formation of Cr (VI) on the surface of ZnO@PAni NRs.

Keywords: conducting polymers; wastewater treatment; Cr (VI) management; nanocomposites; zinc oxide



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1. Introduction

The combined effects of extensive industrialization, population increase, agricultural activity, and other geological and environmental changes have led to an alarming decline in water quality [1–3]. Industries have become a significant contributor to water pollution by introducing harmful chemicals and heavy metals that have a substantial negative impact on both human and animal health, as well as causing widespread ecological harm [4–6]. Among various heavy metals, Cr (VI) has been recognized as a most harmful pollutant, causing various devastating effects such as the irritation and corrosion of human skin; further, it can lead to rust in the textile and metal finishing industries and can interfere with other processes including electroplating, dyeing, wood preservation, painting, fertilizing, and photography [7–11]. Usually in water streams, chromium exists in two different chemical states: Cr (III) and Cr (VI); Cr (VI) is genotoxic and carcinogenic to both humans and animals as compared to Cr (III), which is less toxic [12,13]. Therefore, based on its genotoxic and carcinogenic effects, it has been necessary to develop types of cost-effective and efficient methods which can remove of Cr (VI) from industrial and municipal wastewater. Scientists and researchers have developed various strategical methods such as sedimentation, precipitation, coagulation, flotation, ion exchange, biological treatment, adsorption, and reverse osmosis to reduce environmental problems [14–17]. Among them, adsorption has been preferred as the most effective and efficient method because of its

operational simplicity and environmental friendliness for removing ultra-trace levels of Cr (VI) from wastewater [18–20]. Although adsorption has been proved to be very effective for heavy metal removal, the efficiency of the method depends upon the development of such types of adsorbent materials that can provide an ample number of surface-active sites to bind the heavy metal ions [21].

Recently, metal-oxide-based nanocomposites have been extensively utilized as adsorbent for the removal of heavy metals owing to their large specific surface area, high porosity, ample adsorption sites, and high removal efficiency [22–24]. Various metal oxide nanoparticles such as Fe₂O₃, Fe₃O₄, TiO₂, SiO₂, CuO, CeO₂, and ZnO have been explored in the literature for Cr (VI) removal [1,25–30]. Among these, the ZnO nanoparticle has been recognized as one of the most propitious materials as an adsorbent for the removal of heavy metal ions because of its low cost, high surface area, and optimized electronic structure [25,31]. However, the degree of agglomeration limits these nanoparticles' efficiency, and to address this issue considerable effort has been made in the past to functionalize the surface of ZnO NPs with some electron-donating functional groups such as -OH, -COOH, -SH, -NH₂, etc. [32].

Nowadays, conducting polymers with metal-oxide-based nanocomposite material have become a popular alternative for the sequestration of heavy metals from wastewater because they primarily offer more interfacial surface area for the adhesion of heavy metal ions, are simple to synthesize, and are cost-effective [33]. Polyaniline (PAni) is a highly conducting polymer which has excellent conducting properties and electronic features [34]. PAni has been recognized as one of the cost-effective conductive supports that improve the adsorptive properties of these hybrid nanocomposite materials towards heavy metals through the provision of electron-donating amine and imine groups on the surface of the material [35]. The functional groups and electronic properties in PAni generally involve electrostatic attractions and π - π interactions in the adsorption process which synergistically add on to the efficiency of ZnO NPs [36]. The addition of fillers such as natural clays, metal oxide nanoparticles, etc., can improve the stability of the polymer matrix [37].

Table 1 comprises some of the specific methods for synthesis of ZnO NPs using various modes and their advantages and disadvantages.

Table 1. Synthesis methods of ZnO nanoparticles.

Method	Precursor	Solvent	Features	Advantages/Cost	Disadvantages	References
Chemical coprecipitation	Zinc acetate	Double distilled water	30–60 nm of nanorod	Low energy input/low cost	High cost of precursors	[38]
Microwave decomposition	Zinc acetate dehydrate	1-Butyl-3-methylimidazolium bis (trifluoromethyl-sulfonyl) imide [bmim][NTf ₂]	37–47 nm Sphere	Industrial-scale production/low cost	Parameter control	[39]
Hydrothermal process	Zinc acetate dihydrate	Polyvinylpyrrolidone (PVP)	50–200 nm of nanorod	Uncomplicated equipment/low cost	Nanoparticle stability	[40]
Wet chemical Method	Zinc nitrate hexahydrate	Sodium hydroxide (NaOH) as precursors and soluble starch as stabilizing agent	20–30 nm Acicular	Easy parameter tailoring, low cost	Nanoparticle stability	[41]
Sol-gel method	Zinc nitrate	Distilled water and gelatin as substrate	30–60 nm Circular and hexagonal	Inexpensive and easy to handle chemical reagents		[42]
Solvothermal	Zinc acetate dihydrate	Polyethylene glycol, absolute ethanol	10–20 nm Quasi-spherical	Industrial-scale production	High cost of precursors	[43]
Micro-emulsion	Zn (AOT) ₂	Heptane, diethyl oxalate, chloroform, methanol	10–20 nm Quasi-spherical	Easy parameter tailoring	Surfactant use	[44]
Sono-chemical	zinc nitrate hexahydrate	Potassium hydroxide, cetyltrimethylammonium bromide	200–400 nm flakes	Industrial-scale production	Parameter control	[45]

In the present study, our research group has synthesized ZnO@PAni NRs using an in-situ synthesis approach. Furthermore, adsorption properties of the prepared ZnO@PAni NRs were investigated for the removal of Cr (VI) from an aqueous solution.

2. Experimental Section

2.1. Chemicals

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98% RG), sodium hydroxide pellets (97%, ACS grade), and hydrochloric acid (HCl, 37% ACS grade) were purchased from Sigma Aldrich (St. Luis, MO, USA). Aniline (monomer, 99.5%) and ammonium per sulphate (APS, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 98% RG) were supplied by Alpha Aesar (Somerville, MA, USA). All the chemicals and reagents were used as received without any further purification.

2.2. Synthesis of Zinc Oxide Nanorods (ZnO NRs)

The ZnO NRs were synthesized by the one-pot chemical coprecipitation method reported elsewhere, with some modification [46]. A 0.2 M solution of zinc acetate was prepared in ethanol and under magnetic stirring to attain homogeneity. A 15 mL solution of 0.1 M KOH was added dropwise until the pH of the reaction reached 9–10 and left on magnetic stirring for 12 h. After the stimulated time, the product was collected through centrifuge, washed with deionized water and absolute alcohol in order to remove any unreacted species, dehydrated in a hot-air oven under 90 °C temperature for 3 h, and calcined at 500 °C for another 3 h.

2.3. Synthesis of ZnO Immobilized PAni NRs

A method of oxidative free radical polymerization was utilized for the synthesis of the material reported elsewhere [47]. In a conical flask, a 2% (*w/v*) colloidal solution of ZnO was taken and sonicated for 30 min at 25 °C in an HCl solvent system. After sonication, a solution of 10% (*v/v*) aniline monomer in 0.1 M HCl solution was added to the dispersed colloidal system and magnetically mixed thoroughly to attain a homogeneous condition. After achieving homogeneity, a solid powder of ammonium persulfate of approximately 12.5 g was added to the colloidal mixture prepared above and the reaction was left on ice bath for 12 h. After the stimulated time, the reaction was stopped by adding an excess amount of HCl, and a green-colored precipitate was obtained, which was filtered and washed with deionized water several times to remove unreacted species. The material was dehydrated in a hot-air oven at 80 °C for 4 h.

2.4. Apparatus Used for Characterization

For recording XRD patterns in the current investigation, a powder X-ray diffractometer (XRD) from Rigaku, Tokyo, Japan, was used. Scanning electron microscopy (SEM) photographs of the produced materials were taken using a Zeiss microscope (Jena, Germany). On an Oxford EDX (MA, USA) apparatus coupled to an SEM, research using the energy dispersive X-ray spectroscopy (EDX) technique was carried out. On a Tecnai G2, F30 apparatus, pictures of the acquired samples under a transmission electron microscope (TEM) were taken. TGA analysis was carried out on Perkin Elmer model STA 6000 under an N₂ environment. We used a BRUKER spectrometer to record the Fourier transform infrared (FTIR) spectra of the prepared samples. BET analysis was performed on a BET Surface Area Analyzer quanta chrome, Autosorb iQ2. The remaining concentration of Cr (VI) ions in the solution after adsorption was determined by using an atomic absorption spectrometer (AAS) GBC-908AA.

2.5. Adsorption of Cr (VI) Experiments

The adsorption experiments were performed according to the batch method. An amount of 0.02 g of ZnO@PAni NRs was dispersed in 20 mL of 50 mg/L Cr (VI) solution and was placed in a 50 mL Erlenmeyer flask and shaken into a thermostat water bath at 100 rpm at variable temperature values such as 298 K, 308 K, and 318 K. The effects of

various reaction variables such as contact time (50–200 min), pH of the medium (2–7), and adsorbent dose (12–28 mg) were optimized. The adsorption capacity of the synthesized material was evaluated by using Equation (1):

$$q_e = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (1)$$

where q_e is the amount of Cr (VI) adsorbed per gram of the adsorbent at equilibrium, C_0 and C_e are the initial and final concentration of Cr (VI) ions, respectively, V is the volume of the metal ion solution taken, and W is the mass of the adsorbent taken (g).

The pH of the solution can easily influence the migration of charge on the surfaces of the adsorbent. Therefore, adsorption experiments were performed by varying the pH of the 50 mg/L Cr (VI) solution 15 mg adsorbent dose. The amount of adsorbent has a significant impact on how well metal ions in the solution are able to be absorbed. The effect of various adsorbent doses was optimized for improved adsorption capacity. A variation of adsorbent dose from 12 to 28 mg was used in 20 mL of 50 mg/L aqueous solution of Cr (VI) to investigate the impact of the adsorbent dose on the removal of Cr (VI).

2.6. Effects of Variable Nanorod Size, Initial Cr (VI) Concentration, and Individual Constituents on Adsorption

The effect of varying nanorod size on the adsorption capacity of ZnO@PAni towards Cr (VI) was observed by synthesizing the material with nanorods of various sizes such as 10.5, 19, 32.6, and 52.15 nm. Experiments were performed by taking 20 mL of 50 ppm Cr (VI) solution with 13 mg of the adsorbent dose. The adsorption efficiency of the synthesized material ZnO@PAni was observed towards the variable Cr (VI) concentration from 10 mg/L to 100 mg/L at an optimized reaction condition. Simultaneously the effects of individual constituents, viz. ZnO NRs, PAni, and ZnO@PAni NRs, on Cr (VI) adsorption were also studied at optimized reaction conditions.

2.7. Adsorption Isotherms

The equilibrium attained after the uptake of the metal ion by the adsorbent surface was studied by adsorption isotherms. The present work involves the nonlinear regression analysis of two isotherm models, namely, the Langmuir [48] and Freundlich [49] models, to study the adsorption properties of ZnO@PAni towards Cr (VI).

2.7.1. Langmuir Isotherm

According to the Langmuir model, a reversible chemical equilibrium happens between the ZnO@PAni surface and Cr (VI) ions with a validity of monolayer formation on a surface with a limited number of identical sites, which is nonlinearly represented by Equation (2).

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

2.7.2. Freundlich Isotherm

Equation (3) represents the empirical linear equation pertaining to the Freundlich model, which is based on the idea of a heterogenous surface and reversible multilayer adsorption. The model is nonlinearly represented by Equation (3):

$$q_e = K_F C_e^{1/n} \quad (3)$$

Herein, n is the degree of favorability of adsorption reaction, e.g., if $n > 1$, then adsorption is favorable, while if $n < 1$, then adsorption is non-favorable. K_F (mg/g) is the Freundlich adsorption capacity.

2.8. Adsorption Kinetics

2.8.1. Pseudo-First Order

The adsorption rate is directly proportional to the difference between the equilibrium adsorption capacity and the adsorption capacity at any given time t , according to the pseudo-first-order kinetics model, which is based on the premise that adsorption is regulated by diffusion steps [50],

$$q_t = q_e (1 - e^{-k_1 t}) \quad (4)$$

Herein, q_e = amount of Cr (VI) adsorbed on ZnO@PAni (mg/g) at equilibrium, and q_t = amount of Cr (VI) adsorbed (mg/g) at time t .

2.8.2. Pseudo-Second Order

The following equation provides the linear equation for pseudo-second-order kinetics [51],

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (5)$$

where k_2 = pseudo-second-order rate constant, q_e = amount of Cr (VI) adsorbed on ZnO@PAni (mg/g) at equilibrium, and q_t = amount of adsorbed (mg/g) of Cr (VI) at time t .

2.8.3. Elovich Model

The Elovich equation may be used to understand the sorption kinetics as follows if the process is a chemisorption on highly heterogeneous sorbents [52]:

$$q_t = \frac{1}{\beta} \ln(\alpha \beta t + 1) \quad (6)$$

Herein, α = initial adsorption rate (mg/g·min), β = desorption constant (g/mg), and q_t = adsorption capacity at any time t (mg/g).

2.8.4. Intraparticle Diffusion Model

In a batch reactor system, pore and intraparticle diffusion are frequently rate-limiting when an adsorbent is translocated from the solution into the solid phase of adsorbents [53]. Intraparticle diffusion was investigated using the Weber and Morris equation, as given below:

$$q_t = K_{\text{int}} \times t^{0.5} + C \quad (7)$$

In Equation (12), q_t = amount of Cr (VI) adsorbed (mg/g) at time t , K_{int} = intraparticle diffusion constant (mg/g·min^{0.5}), and t = time.

2.9. Adsorption Thermodynamics

The Gibbs equation and the van't Hoff equation were used to compute thermodynamic parameters such as the Gibbs free energy change (G°), enthalpy change (H°), and entropy change (S°) in order to support our assertion that the adsorption process is endothermic. The equilibrium constant using the Langmuir constant (K_L) is given by Equation (8) [54]

$$K_{\text{eq}} = \frac{K_L \times M_A}{\gamma_e} \quad (8)$$

where K_L is the Langmuir constant (L/mg), M_A is the molar mass of Cr (VI) in mg, and γ_e is the activity of adsorbate, i.e., Cr (VI). For non-ionic species or dilute solutions, $\gamma_e = 1$, so Equation (8) reduces to Equation (9) [55];

$$K_{\text{eq}} = K_L \times M_A \quad (9)$$

The equilibrium constant is related to Gibbs free energy by Equation (10);

$$\Delta G = -RT \ln K_{eq} \quad (10)$$

since

$$\Delta G = \Delta H - T\Delta S \quad (11)$$

Using Equations (10) and (11), we obtained the following:

$$\ln K_{eq} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (12)$$

R = gas constant, K_{eq} = equilibrium constant, and T = temperature of solution. The values of ΔH and ΔS are determined from the slope and intercept of a plot of $\ln K_{eq}$ as a function of $1/T$. The following Equation (11) can be used to compute the free energy change (ΔG) of the adsorption reaction.

2.10. Determination of Point of Zero Charge and Zeta Potential

The point of zero charge (pHpzc) signifies the state of a material when the net electrical charge on its surface becomes zero; at this stage, adsorption takes place through an ion exchange process [56]. To determine the pHpzc, experiments were conducted in a batch mode by taking 20 mL of 0.1 M KCl solution with 50 mg of adsorbent with 10 replicates. The pH of all the 10 samples was adjusted from 1 to 10 using 0.1 M HCl and NaOH solutions. After 24 h, the supernatants were collected using centrifuge and employed to measure the ζ potential of the solution. A curve of ζ potential vs. pH was plotted and is given in Figure S1. The ζ potential was positive till pH 4 and negative from pH 5 to 10. The value of pHpzc was found to be 4.2, which signifies the positive surface of the adsorbent below pH 4.2 and negative surface above pH 4.2.

3. Results and Discussion

3.1. Characterization of ZnO@PAni

Surface morphological properties of the ZnO, PAni, and ZnO@PAni were examined by SEM analysis, and elemental composition was confirmed by EDX. Figure 1a demonstrates the recorded SEM image of PAni which shows flakelike surface structures while the ZnO nanoparticles exhibited a nanowire-type-shaped surface with agglomerations, as presented in Figure 1b. Thus, the SEM investigations suggested that ZnO and PAni possess different surface morphologies as described above. Therefore, it was an interesting thought to utilize the surface properties of both ZnO and PAni to synthesize a composite ZnO@PAni with improved adsorption efficiency. The SEM results of ZnO@PAni indicated that ZnO nanowires are strongly attached on the PAni flakes (Figure 1c). The elemental composition of the prepared ZnO@PAni NRs has been examined by EDX studies, and Figure 1d exhibited the presence of C, N, Zn, and O elements, which revealed the formation of ZnO@PAni NRs with good phase purity. Figure 1e represents the SEM image of ZnO@PAni NRs after the adsorption of Cr (VI), which exhibits a surface covered with small dots on ZnO NRs and PAni flakes, which is due to adsorption of water molecules alongside Cr (VI) ions. Figure 1f represents the EDX spectra of Cr-adsorbed ZnO@PAni NRs, which represent the presence of elements such as C, O, Zn, and Cr. The absence of an N atom from the EDX spectra suggests the involvement of amine and imine groups in the binding of Cr (VI) from the aqueous solution.

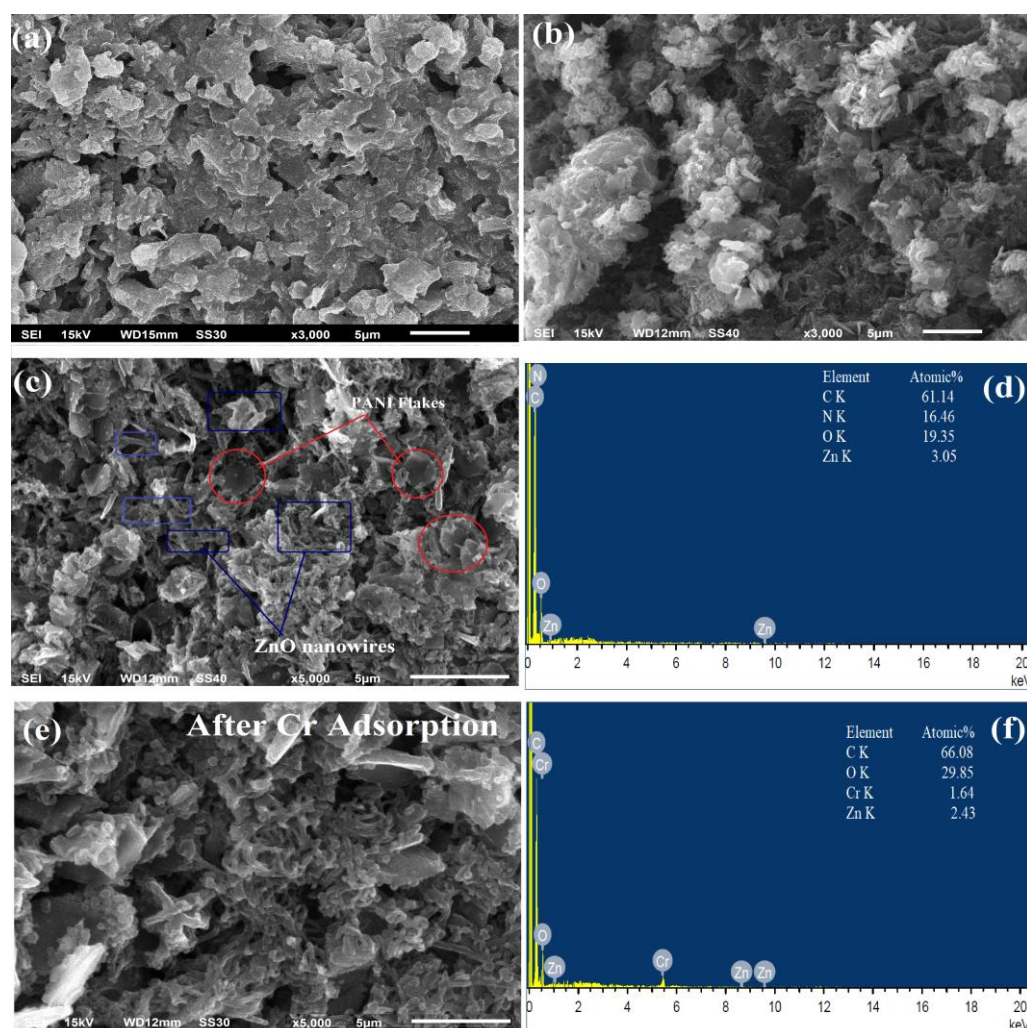


Figure 1. SEM image of (a) PANi, (b) ZnO nanowires, and (c) ZnO@PANi; (d) EDX spectra of ZnO@PANi; (e) SEM image of ZnO@PANi after Cr (VI) adsorption; and (f) EDX spectra of ZnO@PANi-Cr (VI) adsorbed.

The morphological properties of the prepared ZnO@PANi were further authenticated by recording a TEM image. The TEM image of the synthesized ZnO@PANi NRs showed that ZnO nanowires are immobilized with PANi flakes (Figure 2a). Therefore, this confirms the formation of ZnO@PANi NRs using an in situ synthetic method. The Gaussian distribution profiles for average particle size of ZnO@PANi NRs are presented in Figure 2b, which represents the average particle size as 22 nm.

Fourier transform infrared spectroscopy (FTIR) was further used to analyze the type of functional groups formed during processing of the nanocomposite material involving ZnO, PANi, and ZnO@PANi composite and the results are given in Figure 3.

FTIR spectra of ZnO exhibited the presence of various bands at 3443, 1629, 1022, and 443 cm^{-1} . The peak at 3443, 1629 cm^{-1} (stretching and bending vibrational modes of hydroxyl compounds (–OH groups)), and the characteristic peaks at 1022 and 443 cm^{-1} of Zn–O bonds authenticates the formation of ZnO nanorods [57,58]. The FTIR spectrum of PANi exhibits an absorption band at ~829 cm^{-1} (C–H bonding out of plane bending in the benzenoid ring), 515 cm^{-1} (C–N–C bonding mode of aromatic ring), 698 cm^{-1} (C–C and C–H bonding mode of aromatic ring), 1036, 1296, and 1499 cm^{-1} can be attributed to the C–N stretching of the benzenoid ring, and 1576 cm^{-1} may be due to the C–N stretching of the quinoid ring [59]. The FTIR spectrum of ZnO@PANi showed similar characteristics to the band of PANi. However, slight displacement in the peak was observed, which may be

due to the presence of ZnO on the surface of PANi. The band at 3355 cm^{-1} is due to the presence of hydrogen bonding formed between N-H bonds of PANi and oxygen of ZnO NRs [60].

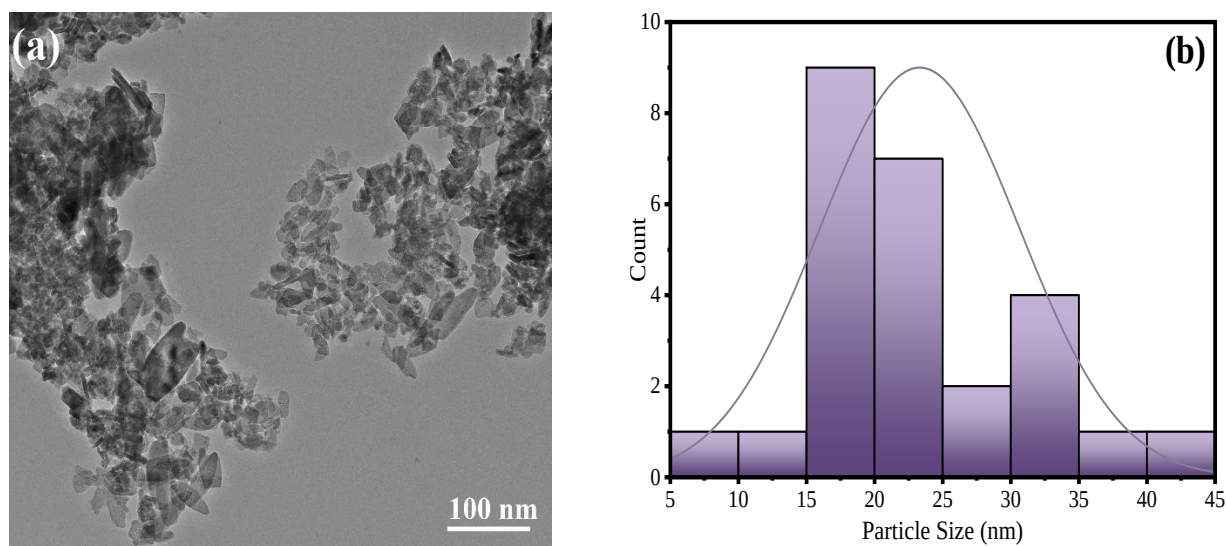


Figure 2. (a) TEM image of ZnO@PANi NRs, and (b) corresponding Gaussian distribution profiles for average particle size.

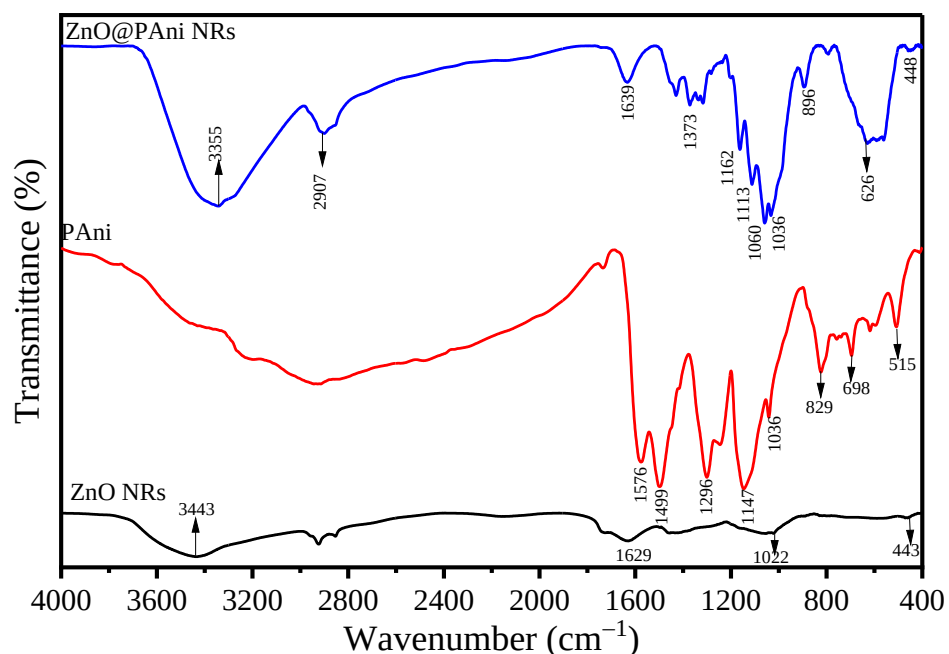


Figure 3. FTIR spectra of ZnO (black line) PANi (red line) and ZnO@PANi NRs (blue line).

Furthermore, recorded XRD data of the ZnO, PANi, and ZnO/PANI are presented in Figure 4. The characteristic peaks of ZnO were observed in the recorded XRD pattern of ZnO, and presence of (011), (100), (002), (101), (020), (102), (302), (110), (103), and (112) diffraction planes confirmed the formation of ZnO corresponding to JCPDS No. 36-1451. The strong diffraction peaks indicated the good crystalline nature of the prepared ZnO. The XRD of PANi has been displayed in Figure 4, and a broad diffraction peak appeared at 25.5° . This is the characteristic peak of PANi and suggests the presence of the (200) diffraction plane in the prepared PANi. The XRD results for ZnO@PANi demonstrated the presence of the (200) diffraction plane of PANi and authenticated the formation of ZnO@PANi [47,61].

However, crystallinity of the ZnO@PAni was reduced due to the amorphous nature of PAni (Figure 4).

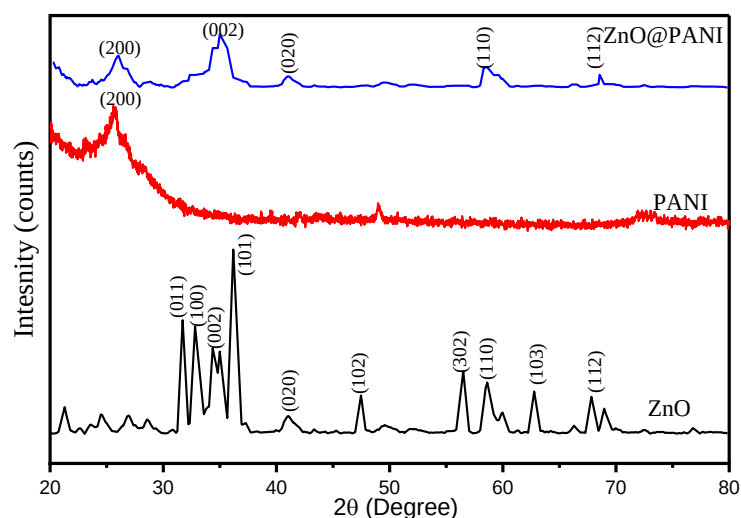


Figure 4. XRD spectra of ZnO (black line) PAni (red line) and ZnO@PAni NRs (blue line).

The thermal stability of ZnO@PAni and PAni were also investigated, and the obtained results are shown in Figure 5. The weight loss for PAni around 124 °C may be attributed to the evaporation of water. The weight loss for PAni at ~700–725 °C was found to be 57.46%. In the case of ZnO@PAni, the weight loss after 700 °C was found to be 44.69%. This shows that weight loss in ZnO@PAni is less compared to pristine PAni. Thus, the introduction of stable ZnO enhances the thermal stability of ZnO@PAni (Figure 5) [62]. The specific surface area of adsorbent plays a vital role, and it is necessary to study the surface area of ZnO@PAni. Brunauer–Emmett–Teller (BET) investigations were carried out to examine the specific surface area of the prepared ZnO@PAni. The nitrogen adsorption–desorption isotherm of ZnO@PAni has been presented in Figure 6a. The BET studies showed that ZnO@PAni has a high surface area of 113.5 m²/g. The pore width distribution curve of ZnO@PAni is shown in Figure 6b. The average pore width of the ZnO@PAni was found to be 7 nm.

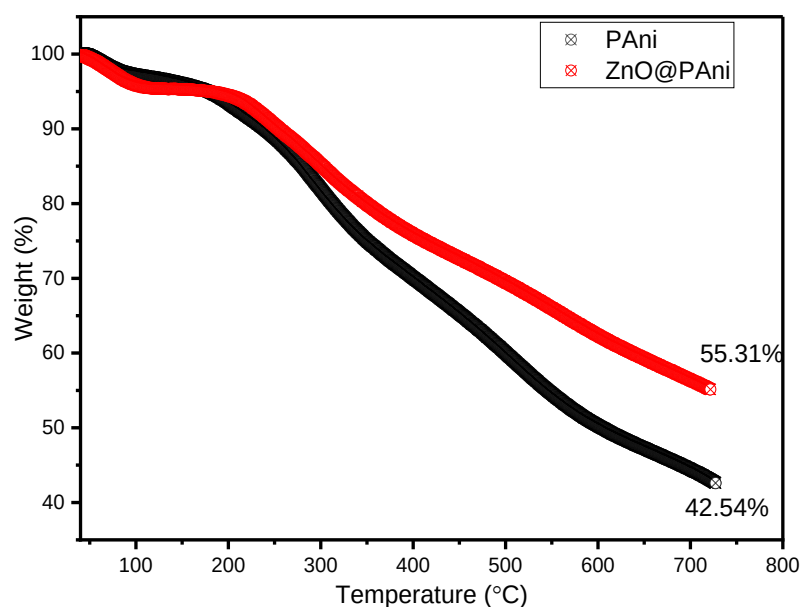


Figure 5. Thermogravimetric (TGA) profile for PAni (black line) and ZnO@PAni (red line).

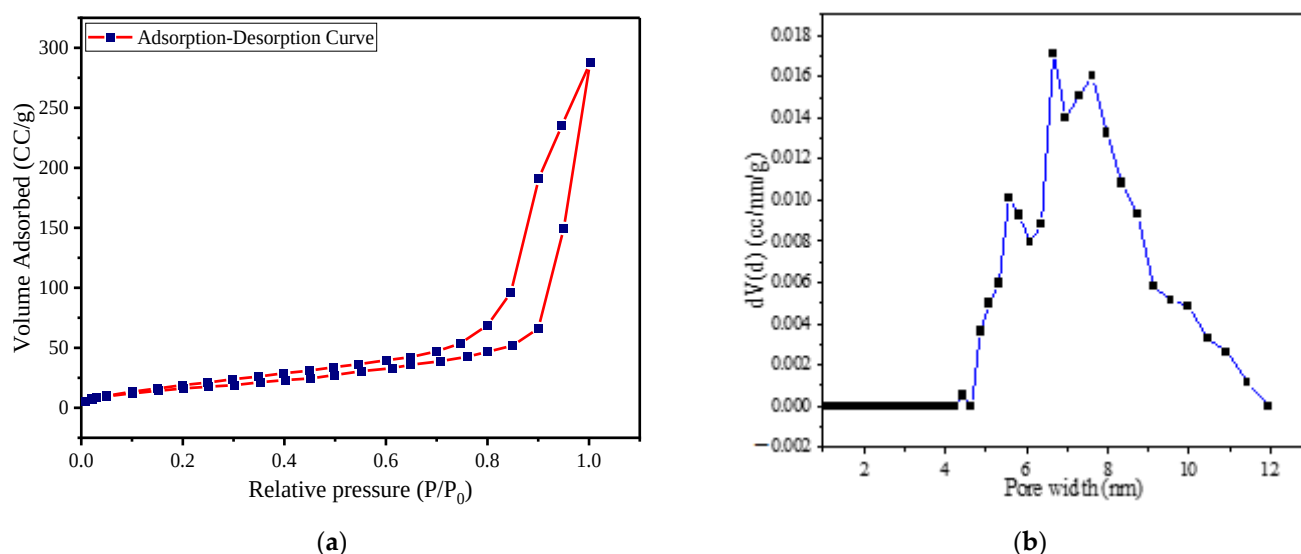


Figure 6. (a) N₂ adsorption–desorption curve, and (b) corresponding BJH pore size distribution curve for ZnO@PAni NRs.

3.2. Adsorption Studies

The adsorption properties of synthesized ZnO@PAni NRs were explored towards Cr (VI) from an aqueous system, the effect of various reaction variables such as pH, adsorbent dose, and contact time were observed, and the results are given in Figure 7a–c. Figure 7a shows the 2D contour plot for the simultaneous interaction of contact time and pH on the adsorption capacity of ZnO@PAni NRs. According to the observations, ZnO@PAni exhibited maximum adsorption capacity for Cr (VI) at pH 2, which continues to decrease with the further increase in pH value. Different forms of Cr (VI) such as CrO_4^{2-} are more prominent in neutral pH, whereas HCrO_4^- is prominent in an acidic medium, which are the key factors for the adsorption of Cr (VI) on the ZnO@PAni surface [63]. Regarding a pH less than 4 ($\text{pH}_{\text{pzc}} = 4.2$, Figure 7d), the adsorbent surface becomes positively charged due to protonation in the presence of an excess of H^+ ions in the solution, and at lower pH, the HCrO_4^- form of Cr (VI) ions predominate. Higher removal efficiency resulted from the strong electrostatic interaction between the positively charged adsorbent surface and the negatively charged HCrO_4^- ions. With increasing pH, deprotonation of the surface of ZnO@PAni can occur due to decreasing H^+ ions [64].

Therefore, at higher pH values, there is less interaction between Cr (VI) ions and adsorbent surface, which leads to lesser adsorption capacity (Figure 7a). The simultaneous effect of contact time (min) on the adsorption of Cr (VI) was also observed in a time span of 50–200 min. Figure 7a shows that >35 mg/g adsorption capacity was observed at 120 min of contact time, and after that a negligible variation was observed with further increase in time, suggesting the occupation of all the surface-active sites or saturation of the adsorbent surface by Cr (VI) ions. Therefore, 120 min was chosen as the optimized time for further adsorption experiments.

The effect of various adsorbent doses was optimized for improved adsorption capacity. The results presented in Figure 7b suggest that the adsorption capacity of ZnO@PAni towards Cr (VI) decreases with an increase in adsorbent dose. The optimized amount of 13 mg is a more suitable adsorbent for Cr (VI) removal, which shows maximum adsorbent capacity. Initially with a lower amount of adsorbent dose, the higher number of surface-active sites are available to bind with Cr (VI) and as a result a high value of adsorbent capacity is achieved. At a higher adsorbent dose, due to the agglomeration of nanoparticles, a smaller number of surface-active sites are available and as a result a lower value of adsorbent capacity occurs [65]. Furthermore, we have also investigated the adsorption capacity by varying the pH and adsorbent dose, and the observations indicated that the

highest adsorption capacity of more than 50 mg/g for 13 mg ZnO@PAni in an aqueous solution of pH 2 (Figure 7c) was achieved. Therefore, it was concluded that ZnO@PAni has the potential to adsorb the Cr (VI) effectively. To further confirm the adsorption of Cr (VI) by ZnO@PAni, we have recorded a SEM image of the ZnO@PAni surface after Cr (VI) adsorption. Figure 1e shows the recorded SEM image of ZnO@PAni with Cr (VI) adsorption. The Cr (VI) particles are seen on the surface of ZnO@PAni. The presence of Cr (VI) on ZnO@PAni was also further authenticated by EDX. Figure 1f shows the obtained EDX data of Cr (VI)-adsorbed ZnO@PAni. The EDX data reveal the presence of Cr, C, Zn, and O elements. Thus, it is confirmed that Cr (VI) particles are present on the ZnO@PAni surface. This confirms the adsorption properties of ZnO@PAni nanocomposite.

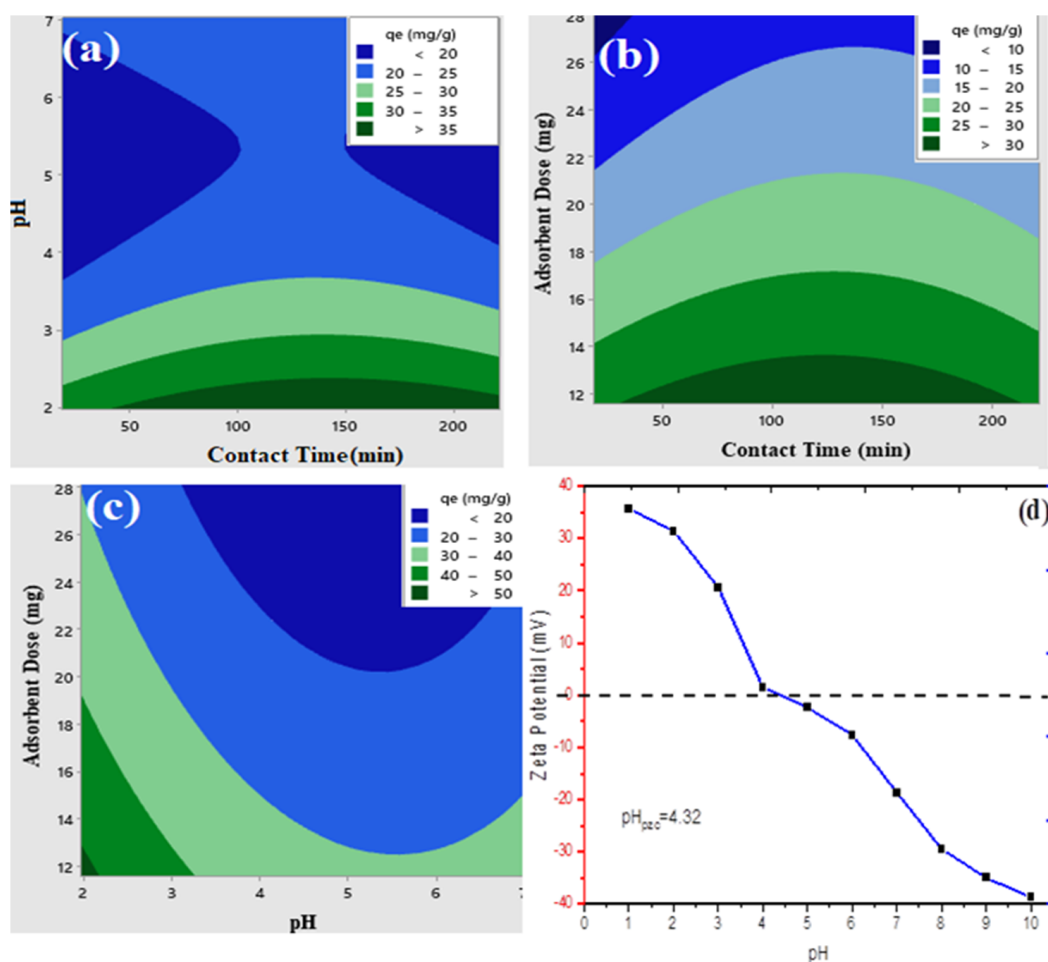


Figure 7. The 2D contour plots for optimization of process variable: (a) pH vs. contact time, (b) adsorbent dose vs. contact time, and (c) pH vs. adsorbent dose for removal of (50 mg/L) Cr (VI) by ZnO@PAni; (d) pH vs. zeta potential curve for the determination of the point of zero charge (pH_{pzc}).

3.3. Effect of Varying Nanorod Size, Initial Cr (VI) Concentration, and Individual Adsorbent Material

The effect of varying nanorod size on the adsorption capacity of ZnO@PAni towards Cr (VI) was observed, and the obtained results are summarized in Figure 8a. The observations demonstrated that with the increase in nanorod size from 10.5 to 20 nm, adsorption capacity of ZnO@PAni increased from 25.56 to 37.93 mg/g, while beyond 20 nm, a gradual decrease in adsorption capacity was observed, which might be due to the lower surface area possessed by larger-size nanorods [66]. Initially, at 10.5 nm nanorod size, there may be a possibility of stacking of nanorods due to small size and hence a lower adsorption

capacity was observed. As the particle size increased to 19 nm, the possibility of agglomeration decreased, and as a result, nanorods were distributed throughout the aqueous media and thus a high adsorption capacity was achieved. At a higher particle size, due to low surface area, a smaller number of surface-active sites were available and hence a decrease in adsorption capacity was constantly observed. The adsorption efficiency of the synthesized material ZnO@PAni was observed towards the variable Cr (VI) concentration and the obtained results are summarized in Figure 8b. The observations and results suggested that with gradual increase in Cr (VI) concentration from 10 mg/L to 100 mg/L, the adsorption capacity of ZnO@PAni also increases. This can be explained as the adsorbent consists of plenty of surface-active sites that can easily accommodate Cr (VI) ions, even at a 100 mg/L concentration. Figure 8c represents the adsorption capacity bars with respect to the synthesized material (ZnO@PAni) and its constituent materials, including ZnO and PAni. It was observed that the composite formed by assembling ZnO and PAni results in higher adsorption capacity as compared to its individual constituents. This is due to the synergistic effect provided by -OH groups on the surface of ZnO and -NH₂ groups on PAni that provide plenty of charge density to bind the positively charged Cr (VI) [67,68].

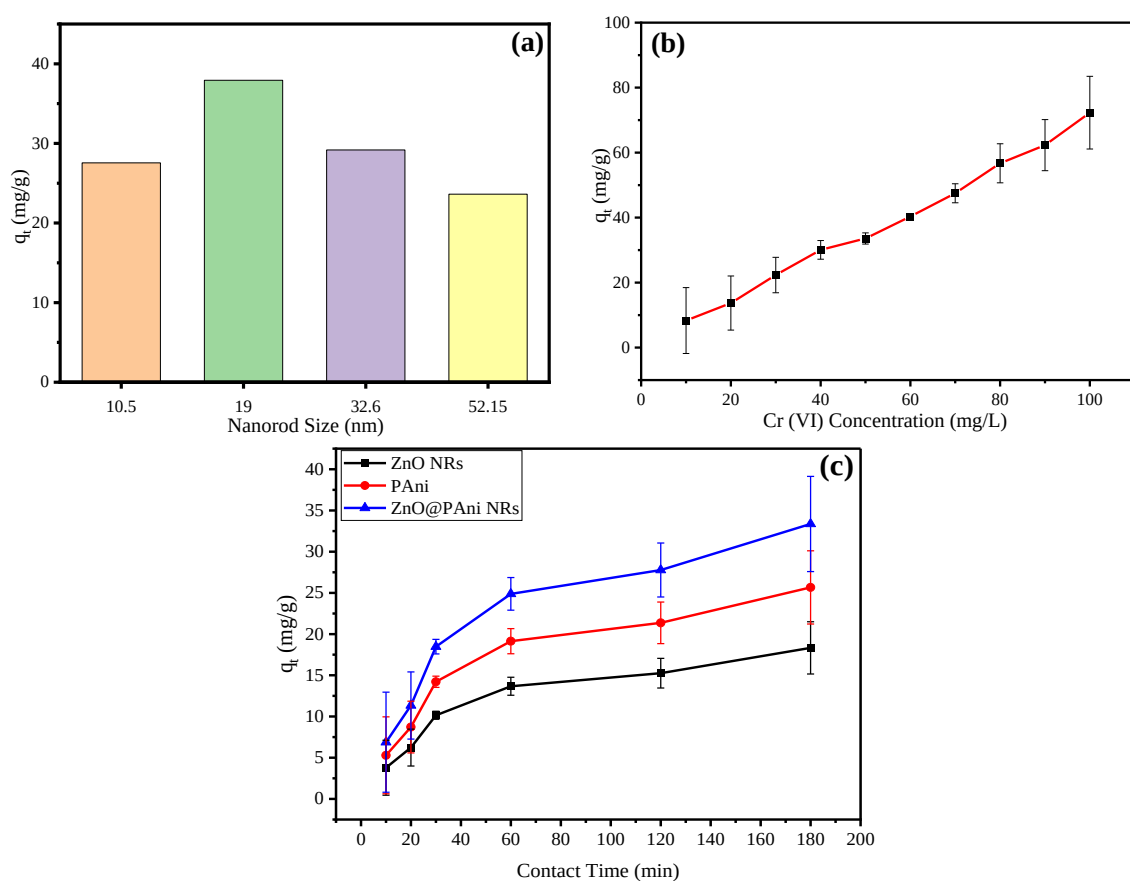


Figure 8. Variation of adsorption capacity of ZnO@PAni with respect to (a) particle size, (b) initial Cr (VI) concentration, and (c) the synthesized material and its constituents.

3.4. Adsorption Isotherm Studies

The equilibrium data obtained after experiments were applied to the nonlinear models of Langmuir and Freundlich, and the results are given in Table 2 and Figure 9a,b. Table 2 shows that with a low value of chi square ($\chi^2 = 3.41$) and high value of R^2 (0.99), the Langmuir model was found to be the best model for explaining the adsorption of Cr (VI) on ZnO@PAni. The maximum monolayer adsorption capacity was found to be 142.27 mg/g at 298 K, 219.18 mg/g at 308 K, and 310.47 mg/g at 318 K. The Langmuir constant K_L was found to be 0.412, 0.767, and 0.849 L/mg at temperatures from 298 to 318 K. The significance

of the KL value also establishes the affinity of adsorbent towards adsorbate, and in this case, as the temperature increases, the value of K_L also increases, suggesting a high affinity of ZnO@PAni NRs towards Cr (VI) and a high value of adsorption capacity achieved at high temperature. The Freundlich adsorption parameters were calculated from the nonlinear plot between q_e versus $\ln C_e$ presented in Figure 9b and given in Table 2, which shows that the values of n are >1 for all temperature ranges, indicating good adsorption. The values of n being greater than 1 suggest the existence of a substantial interaction between the ZnO@PAni surface and Cr (VI) ions and the gradual increase in the value of 1 with temperature suggests high favorability of adsorption at high temperature. The obtained results through nonlinear regression for Langmuir and Freundlich models also suggest the data are statistically valid for explaining the adsorption behavior of ZnO@PAni NRs towards Cr (VI) [69,70].

Table 2. Adsorption isotherm parameters for the removal of (100 mg/L) Cr (VI) on ZnO@PAni NRs at 298 K, 308 K, and 318 K.

Model	Parameters	298 K	308 K	318 K
Langmuir	q_m (mg/g)	142.27	219.18	310.47
	K_L (L/mg)	0.412	0.767	0.849
	R^2	0.99	0.99	0.99
	χ^2	4.13	3.55	3.41
Freundlich	K_F (mg/g) (mg/L) $^{1/n}$	109.79	111.17	121.44
	n	1.84	2.52	3.42
	R^2	0.98	0.97	0.96
	χ^2	21.61	19.04	15.13

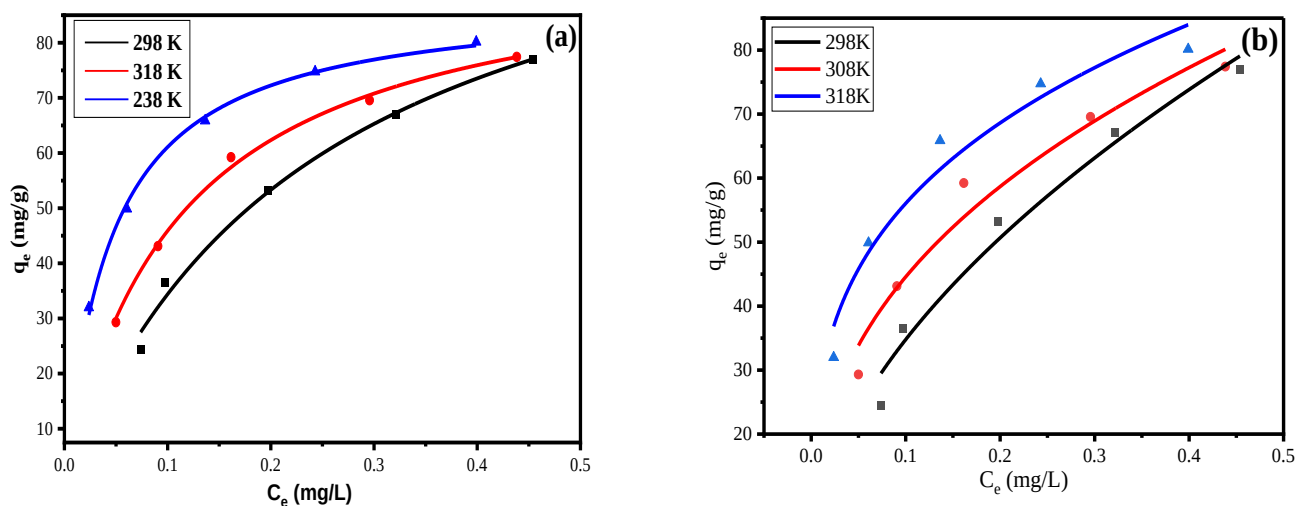


Figure 9. Nonlinear regression fitted adsorption isotherms of (a) Langmuir and (b) Freundlich using 20 mL of 100 mg/L Cr (VI) solution at pH 2 and 13 mg of adsorbent dose at 298–318 K temperature range.

3.5. Adsorption Kinetics

The kinetic data obtained from the kinetic studies are listed in Table 3, and graphs are given in Figure 10a,b. The high value of correlation coefficients $R^2 = 0.99$ and low value of $\chi^2 = 0.36$ characterized the pseudo-second-order kinetic model best describing the sorption rate of Cr (VI) on the surface of ZnO@PAni. According to the pseudo-second-order kinetic model, chemical adsorption may be the rate-limiting phase, and there may be entilement of valence forces through the electron deficient Cr (VI) orbitals and electron rich $-NH_2$ and $-OH$ groups, which can involve a complex reaction involving chemical bond formation

and diffusion reactions simultaneously [71]. Moreover, the obtained q_e (calculated values) for PSO are found to be ore closer to the q_e (experimental values). According to The Weber–Morris equation, if the adsorption rate is controlled by the intraparticle diffusion process, then the plot between q_t and $t^{0.5}$ will be a straight line. Figure 10b represents the intraparticle diffusion plot between q_t and $t^{0.5}$ which showed a multilinear plot which does not pass through the origin, suggesting the involvement of boundary-layer diffusion in Cr (VI) adsorption. The first linear portion with a k_{p1} value of 5.02 represents the rapid external diffusion of Cr (VI) to the ZnO@PAni surface and second portion with k_{p2} value of 1.48 corresponds to the intraparticle diffusion effect.

Table 3. Kinetic parameters for the removal of 50 mg/L Cr (VI) on ZnO@PAni NRs at optimized reaction condition.

Model	Parameters	318 K
Pseudo-first order	$q_{e,exp}$ (mg/g)	35.69
	$q_{e,cal}$ (mg/g) k_1 (1/min)	41.36
	R^2	0.98
	χ^2	1.63
Pseudo-second order	$q_{e,exp}$ (mg/g)	35.69
	$q_{e,cal}$ (mg/g) k_2 (g/mg $\times$ min)	36.27
	R^2	0.99
	χ^2	0.36
Elovich	α (mg/g $\times$ min)	1.64
	β (g/mg)	0.089
	R^2	0.96
	χ^2	2.36
Intraparticle diffusion	k_{p1} (mg/g $\times$ min ^{1/2})	5.02
	k_{p2} (mg/g $\times$ min ^{1/2})	1.48
	R_1^2	0.98
	R_2^2	0.96
	χ^2	1.38

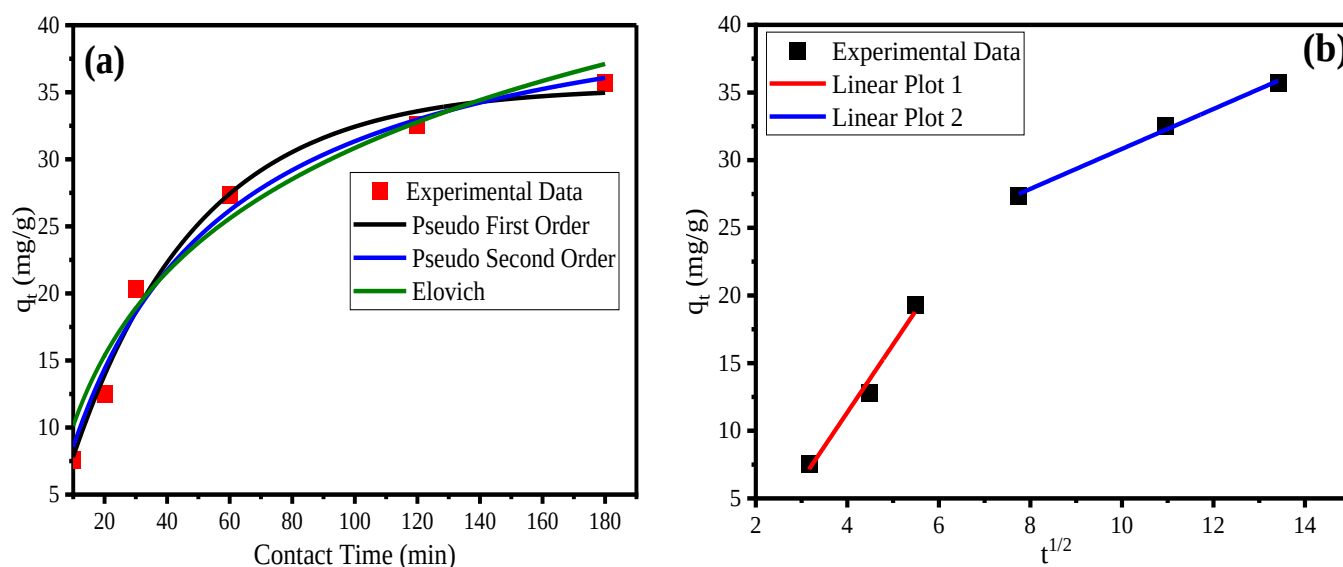


Figure 10. (a) Nonlinear fitted kinetic curves for pseudo-first order, pseudo-second order, and Elovich model, and (b) linear plot of intraparticle diffusion.

3.6. Adsorption Thermodynamics

Table 4 and Figure 11 provide a list of the thermodynamic characteristics related to the adsorption of Cr (VI) on the ZnO@PAni surface.

Table 4. Thermodynamic parameters for the removal of Cr (VI) on ZnO@PAni NRs at 298 K, 308 K, and 318 K.

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol·K)
298	−23.79	32.01	0.187
308	−25.67		
318	−27.54		

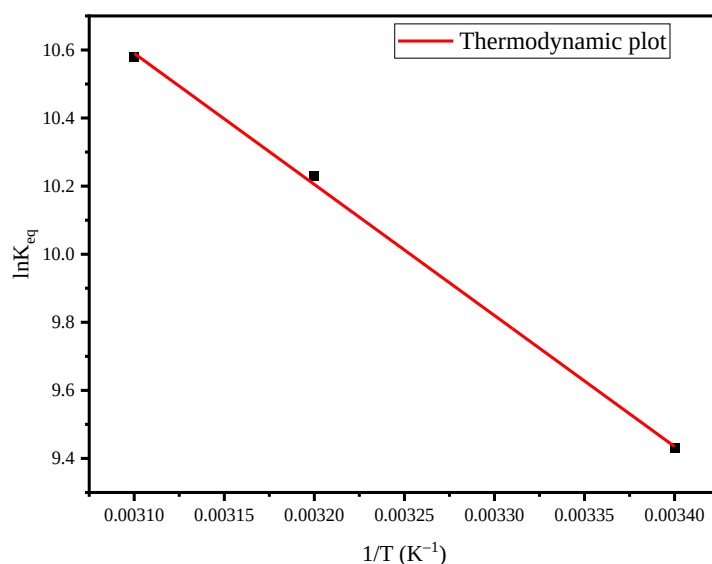
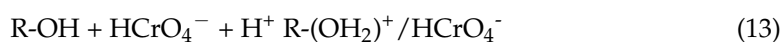
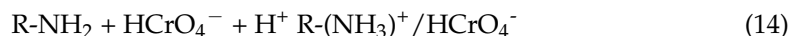
**Figure 11.** Adsorption thermodynamics curve for evaluation of enthalpy and entropy of the reaction.

Table 4 shows that the value of ΔH° is found to be 32.01 kJ/mol, which suggests that the adsorption of Cr (VI) on ZnO@PAni is endothermic in nature. Owing to this explanation, the adsorption reaction is highly favorable at a high temperature, i.e., 318 K, and less favorable at 298 K. The entropy ΔS° was found to be 0.187 kJ/mol $\times$ K, which is also positive, suggesting a randomness created in the system. The Gibbs free energy value ΔG° was found to be −23.79 kJ/mol at 298 K, −25.67 kJ/mol at 308 K, and −27.54 kJ/mol at 318 K, which suggests the feasible nature of the adsorption reaction and increase in negative magnitude with temperature, suggesting high feasibility at high temperature [72].

3.7. Adsorption Mechanism

From the kinetic and isotherm studies, it was observed that both adsorbent and adsorbate govern the adsorption process and as the time progresses, more and more portions of surface-active sites on the adsorbent surface are occupied accordingly. The pseudo-second-order model revealed the primary rate-controlling step as the adherence of Cr (VI) on the surface of ZnO@PAni. Additionally, the intraparticle diffusion also suggested the involvement of boundary-layer diffusion in Cr (VI) adsorption. The first step is ascribed as the mass transfer of Cr (VI) to the adsorbent surface, and the second step is attributed as the diffusion process through the inner nanopores of adsorbent. From the FTIR and SEM-EDX analysis, it was confirmed that the adsorbent surface is rich with electron-donating functional groups such as -OH and -NH₂ groups, which are involved in the adsorption process by the following Equations (13) and (14). Figure 1f shows the obtained EDX data of Cr (VI)-adsorbed ZnO@PAni. The EDS data reveal the presence of Cr, C, Zn, and O elements. Thus, it is confirmed that Cr (VI) particles are present on the ZnO@PAni surface. This confirms the adsorption properties of ZnO@PAni nanocomposite.





3.8. Comparison with the Literature

The adsorption studies of the synthesized material ZnO@PAni were compared with other ZnO-based nanocomposite materials reported in the literature and are listed in Table 5. It was observed from the comparison data that modification of ZnO with PAni results in enhanced adsorption capacity towards Cr (VI) as compared to other materials.

Table 5. Comparison of the adsorption performance of present study with literature.

Adsorbent	Cr (VI) Removal Capacity (mg/g)	pH	Contact Time (min)	References
CuO–ZnO–C	201.56	2	600	[68]
ZnO-MWCNTs	152.2	2	120	[73]
rGO-ZnO	25.45	3	240	[74]
Ag/ZnO-AC	4.17	2.5	1200	[75]
PA/TSC-ZnO	90.83	4	250	[76]
GO ZnO-ZnFe ₂ O ₄	109.89	4	120	[77]
GO-CS@MOF	144.92	2	360	[78]
[Zn(BDC)(DMF)]	310.47	2	120	Present study

4. Conclusions

In summary, a multifunctional nanocomposite material using PAni and ZnO nanorods was synthesized through a free radical oxidative polymerization reaction. Various spectroscopic and morphological studies confirmed the successful formation of the material. The FTIR studies suggested the formation of H bonding between ZnO and -NH₂ groups of PAni. The XRD results for ZnO@PAni demonstrated the presence of the (200) diffraction plane of PAni with characteristic peaks of ZnO. The TEM image of the synthesized ZnO/PAni composite showed that ZnO nanowires are linked to the flakelike PAni with an average particle size of 22 nm. The synergistic effect of solid ZnO NRs in the polymer matrix results in high thermal stability of PAni. The BET studies showed that ZnO@PAni has a high surface area of 113.5 m²/g with average pore width of 7 nm. The material as an adsorbent showed high affinity towards Cr (VI) from an aqueous solution at optimized reaction conditions of pH 2 and 13 mg adsorbent dose. The adsorption reaction was highly pH dependent and the obtained data were best explained by the Langmuir model, resulting in maximum monolayer adsorption capacity (*q_m*), as 142.27 mg/g at 298 K, 219.18 mg/g at 308 K, and 310.47 mg/g at 318 K were obtained. The kinetic studies suggested the uptake of Cr (VI) by ZnO@PAni NRs was best supported by a pseudo-second-order model, indicating a chemical bond formation between Cr (VI) and the adsorbent surface. In future, we plan to utilize the adsorptive and optical properties of the material towards Cr (VI)-polluted wastewater, splitting the simultaneous hydrogen production reaction under UV-Vis light radiations. Thus, the synthesized nanomaterial could emerge as cost-effective and highly efficient towards sustainable wastewater management and energy production.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w15101949/s1>, Figure S1: Point of zero charge (pHpzc) analysis using Zeta potential; Figure S2: Non-linear regression for (a) Langmuir (b) Freundlich and (c) Temkin isotherms at 298 to 318 K temperature. Table S1: Adsorption isotherm parameters for the removal of (100 mg/L) Cr (VI) on ZnO@PAni NRs at 298 K, 308 K and 318 K obtained by non-linear regression analysis.

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