Polyaniline and Phosphotungstic acid Doped Composite Catalyst for Visible-Light Photocatalytic Degradation of Phenol

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Abstract

Photosensitizer functionality of conducting polyaniline (PANI) and homogeneous catalysis of polyoxometalates, if coupled, could open a new avenue of efficient visible light photocatalyst. Incorporating this objective in the present work, new photocatalysts were prepared and investigated for visible light degradation of phenol. By chemical polymerization method the following four materials viz., PANI, PANI-PVP (Poly(vinyl pyrrolidone)), PANI-PTA (phosphotungstic acid) and PANI-PTA-PVP were synthesized. XRD, SEM, UV-vis and FTIR spectra showed the interaction of PANI with other components. Haber inner irradiation type photoreactor with 0.33 to 0.83 g L⁻¹ suspended catalyst (300 ml volume; 10 to 70 ppm phenol concentration) in the pH range of 2 to 8 under visible light from 150 W tungsten halogen lamp was used. PANI, PANI-PVP, PANI-PTA and PANI-PTA-PVP exhibited the phenol decomposition of 6.8, 10.0, 27.6 and 56.7 % respectively at optimal condition of catalyst dosage of 0.50 g L⁻¹, pH 4, initial phenol concentration of 50 ppm; 2 ml H₂O₂ and constant air flow. The combined effect of PVP and PTA played a vital role in enhancing the photocatalytic activity of PANI in visible region. Hence, the three component catalyst PANI-PTA-PVP emerged as the most efficient catalyst.

Keywords: Polyaniline, Poly(vinyl pyrrolidone), Chemical polymerization, Phosphotungstic acid dopant, Phenol photodegradation.
1. INTRODUCTION

Intrinsically conducting polymers, such as polyaniline (PANI), polythiophene, polypyrrole etc., have become prominent because of their specific advantageous properties. Among the conducting polymers PANI has witnessed a great deal of attention because of its unique electrical, structural and optical properties [1]. The application of PANI has been extended to various fields such as, sensors [1], energy storage devices [2], anticorrosion coatings [3], solar cells [4], memory devices [5], catalyst [6] etc.

The application of Polyoxometalates (POM) [7] are primarily on their redox properties, ionic weights, photochemical response, medicine, molecular materials and conductivity. The majority of the applications of POMs are found in the area of catalysis [8]. Heteropoly acid (HPA) is one type of POM. HPA is a common reusable acid catalyst in photochemical reactions. The HPAs are widely used as homogeneous and heterogeneous catalysts [9]. By combining a conducting polymer such as PANI and a HPA, a composite can be formed. In particular, the anchoring of HPA within the network of PANI leads to the formation of composite materials in which the inorganic clusters keep their integrity and activity while taking benefit from the organic part [10]. Different conducting polymer-HPA composites have been prepared by chemical oxidation [10] route. The dispersion of the phosphotungstic acid (PTA- a HPA) throughout a polymer matrix has been shown to enhance the stability and the catalytic activity [11] relative to those of a PTA in its pure crystalline state.

When Poly(vinyl pyrrolidone) (PVP) forms intermolecular H-bond with growing PANI chain, it can control the stereochemistry of the polymer molecule and ultimately the PANI particle size and morphology. Hence PVP is termed as a soft template [12] and acts as a steric stabilizer. Addition of PVP improves the properties of PANI composite [13].

The wide spread occurrence of phenols and phenolic compounds in waste water lead to serious environmental toxicity hazard [14]. So far, several treatment methods [15] such as chemical oxidation, biological digestion, ozonolysis, wet oxidation and activated carbon adsorption are applied for the removal of phenol from industrial effluents. However, each of these methods has some limitations. In the past decades a new treatment technology, known as Advanced Oxidation Processes (AOP) [16] capable of the destruction of wide range of organic compounds was developed. AOPs rely on in-situ production of highly reactive hydroxyl radicals for degradation. Hydroxyl radicals are produced from H$_2$O$_2$ with the help of catalysts. The present investigation is focused on the synthesis of chemically polymerized PANI with PTA doping and without/with structure-directing template, PVP. Four materials PANI, PANI-PVP, PANI-PTA and PANI-PTA-PVP were synthesized and investigated for photocatalytic decomposition of phenol under visible light. Influence of different
parameters such as phenol concentration, pH and dose of catalyst on phenol degradation was investigated.

2. EXPERIMENTAL

2.1. Materials

Phosphotungstic acid (PTA) was obtained from Sigma-Aldrich and used without further purification. Aniline from Merck was distilled prior to use. Water was used after two distillations (DDW), Con. HCl, PVP, hydrogen peroxide, N-methyl pyrrolidone (NMP) and acetone were obtained from Merck. Sodium carbonate and Folin-phenol reagent were obtained from Spectrum Chemicals.

2.2. Synthesis of PANI materials

PANI was synthesized by chemical polymerization using hydrogen peroxide as the oxidant [17]. In the present study 2 ml aniline, 2 ml H\textsubscript{2}O\textsubscript{2}, 2 ml Con. HCl and 94 ml DDW were taken in a 250 ml beaker and the mixture was stirred for the completion of polymerization reaction. The polymer mass formed was separated, washed several times with 0.1 M HCl, distilled water and acetone until the washings became colourless. The sample was dried in an air oven at 110°C, ground into fine powder and stored in polythene packet. Similarly PANI-PTA and PANI-PVP were prepared by adopting the same procedure as chemical polymerization with PTA (PANI-PTA: [PTA] = 5 mM) and with PVP (PANI-PVP: [PVP] = 10 mM). PANI–PTA-PVP composite was synthesized by adopting the same procedure as above with PTA and PVP.

2.3. Characterization

The UV-vis absorption spectra of all the polymer samples in NMP solvent were obtained by scanning the wavelength in the range of 330-1100 nm on Perkin Elmer UV-vis spectrophotometer (Lambda 25 model), with matched 1cm quartz cuvettes. FTIR spectra of all PANI materials in KBr pellets were recorded with JASCO FTIR – 410, spectrophotometer in the region of 4000-400 cm\textsuperscript{-1}. Powder X – ray diffraction patterns of all PANI materials were recorded using a Shimadzu XRD 6000 X-ray diffractometer with Cu-K\alpha radiation source (λ = 1.54 Å) operated at 40 kV and 30 mA in the 2θ range 10-90° at the scan speed of 10.0° per minute. Surface morphologies of the powder polymer samples were observed with JEOL JSM – 6390 Scanning Electron Microscope (SEM) operating at 20 kV, after coating the samples with platinum for 45 s using JEOL JFC-1600 auto-fine coater with sputtering technique.
2.4. Photocatalysis

To analyse the photocatalytic behavior of PANI and its composite materials, Haber inner irradiation type photoreactor with 150 W tungsten-halogen lamp, model HIPR-LC-150 and light intensity = 14.79 mW/cm² at 555 nm measured with Kusem – Meco Luxmeter, model KM Lux 200 K) was used. The photoreactor was covered with aluminium foil during shaking and the course of reaction in order to prevent fall of indoor light on reactor. Phenol solution (300 ml) and the photocatalyst were fed into the reactor. The pH of the medium was adjusted using 0.1 M HCl or NaOH. Air flow at constant rate was made using air pump. All the experiments were carried out at the temperature of 28±2°C and atmospheric pressure. 300 ml phenol solution was mixed thoroughly with required quantity of photocatalyst and shaken for 30 minutes to reach dark equilibrium in the absence of light. The first sample was taken to determine the initial concentration of phenol solution. After that tungsten lamp was switched on to initiate photocatalysis. At various time intervals for 160 min, 2 ml sample was drawn out for every 10 min for an hour and remaining samples were taken at 20 min intervals. The samples were centrifuged and filtered using Whatman filter paper No. 1 to remove the suspended solids. Photodegradation study for the four catalysts PANI, PANI-PVP, PANI-PTA and PANI-PTA-PVP were carried out in light, constant air flow, H₂O₂ 2 ml, at initial phenol concentration of 50 ppm, pH 4 and dose of catalyst of 0.5 g L⁻¹. Experimental variables like initial phenol concentration, pH, and dose of catalyst were investigated.

Phenol concentration was analysed by using Phenol-Folin method [18]. In this method 2 ml of phenol aliquot was mixed with 0.5 ml of Phenol-Folin reagent and 2 ml of sodium carbonate (20 % solution) and diluted to 10 ml using DDW. The mixture was heated in a water bath for one minute to develop a blue colour. After 10 min of incubation, absorbance was measured at λ_max = 650 nm. The % photodegradation of phenol was calculated using equation (1).

\[
\text{% Degradation} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]

Where C₀ and Cₜ are the initial concentration and the concentration of phenol after irradiation time (t) respectively.

3. RESULTS AND DISCUSSION

3.1. UV-vis spectral studies

The electronic spectra of PANI and its composites in NMP solvent are displayed in Fig. 1 and the spectral data in Table 1. PANI and its composites have three significant peaks with changes in intensities and peak positions. PANI shows three characteristic absorption peaks [19] one at 380 nm, another broad band around 557 nm and weak broad band above 678 nm. They are attributable to π- π* transition, low wavelength
polaron - $\pi^*$ transition and the high wavelength polaron - $\pi^*$ transition band respectively [19,20]. PANI – PVP exhibits three peaks in the region of 369 nm, 549 nm and broad band above 687 nm. The first two peaks shift to lower wavelength due to heavy interaction of PVP with PANI [13]. PANI doped with PTA shows three absorption bands at 380 nm, broad band around 543 nm and above 686 nm. By the interaction of PTA with PANI the second peak moves to lower wavelength and third peak moves to higher wavelength, but both peaks have decrease in intensity. PANI-PTA-PVP composite has the lowest wavelength $\pi$- $\pi^*$ peak at 365 nm and the longest wavelength polaron - $\pi^*$ band at 719 nm. These shifts in peak positions indicate the interaction between the components [19,20] and confirm the formation of composites.

![Fig.1. UV-vis spectra of PANI and its composites in NMP solvent](image)

(a) PANI (b) PANI-PVP (c) PANI-PTA and (d) PANI-PTA-PVP

**Table 1.** UV-vis spectral and XRD data for PANI and its composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>UV-vis peaks in NMP solvent (nm)</th>
<th>XRD data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2θ</td>
</tr>
<tr>
<td>PANI</td>
<td>380, 557, 678</td>
<td>18.5</td>
</tr>
<tr>
<td>PANI-PVP</td>
<td>369, 549, 687</td>
<td>28.1</td>
</tr>
<tr>
<td>PANI-PTA</td>
<td>380, 543, 686</td>
<td>26.3</td>
</tr>
<tr>
<td>PANI-PTA-PVP</td>
<td>365, 547, 719</td>
<td>28.5</td>
</tr>
</tbody>
</table>
3.2. FTIR spectral studies

FTIR spectra of PANI and its composites are shown in Fig. 2 and the spectral data are entered in Table 2. PANI and its composites have more or less the same peaks/bands with small changes in position and intensities. In PANI the characteristic absorption bands are found at 833, 1186, 1287, 1351, 1442, 1500 and 1566 cm$^{-1}$ corresponding to C–H out-of-plane bending vibration for aromatic rings, C–H in-plane bending vibration, C = N stretching vibration in quinoid, stretching of imine, stretching forms of C–N bond, C=C stretching vibration of benzene ring and C=C stretching vibration of quinoid respectively [13, 19, 20]. The IR spectra for PANI – PVP composite show the characteristic peaks at about 1575, 1494, 1447, 1388, 1282, 1167 and 831 cm$^{-1}$. All the characteristic peaks of PANI are shifted slightly in PANI – PVP composite, indicating that there is strong interaction between these two components. The spectra of PANI – PTA possess peaks at 1572, 1500, 1444, 1385, 1285, 1155, 1079, 979, 891 and 818 cm$^{-1}$. The new peak at 1079 cm$^{-1}$ is assigned to stretching mode of P–O bond, at 891 cm$^{-1}$ to the W = O terminal bond and finally at 818 cm$^{-1}$ to C–H out plane bending vibration of PANI [21]. Therefore the above result shows that PTA is completely interacting with PANI and forms the new composite [21]. In PANI – PTA – PVP composite, the characteristic shifted vibrations are as follows from 979 cm$^{-1}$ to 971 cm$^{-1}$ of W = O bond of PTA in the composite and W – O – W band from 891 to 893 cm$^{-1}$. Thus the interaction of PTA and PVP with the polymer matrix is confirmed.

Fig. 2. FTIR spectra of (a) PANI, (b) PANI-PVP (c) PANI-PTA and (d) PANI-PTA-PVP
### Table 2. FTIR spectral peak positions (in cm\(^{-1}\)) of (a) PANI, (b) PANI-PVP, (c) PANI-PTA and (d) PANI-PTA-PVP

<table>
<thead>
<tr>
<th></th>
<th>PANI</th>
<th>PANI-PVP</th>
<th>PANI-PTA</th>
<th>PANI-PTA-PVP</th>
<th>FTIR peak assignment</th>
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<tr>
<td>833</td>
<td>831</td>
<td>818</td>
<td>821</td>
<td>C-H out plane bending vibration</td>
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<tr>
<td>891</td>
<td>893</td>
<td></td>
<td></td>
<td>Asym. Stretching (W-O-W)</td>
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<tr>
<td>979</td>
<td>971</td>
<td></td>
<td></td>
<td>Stretching (W=O)</td>
<td></td>
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<tr>
<td>1079</td>
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<td></td>
<td></td>
<td>Stretching P-O</td>
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<tr>
<td>1186</td>
<td>1167</td>
<td>1155</td>
<td>1113</td>
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<td>1285</td>
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<td>C=N stretching vibration in quinoid</td>
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<tr>
<td>1566</td>
<td>1575</td>
<td>1572</td>
<td>1581</td>
<td>C=C stretching vibration of quinoid</td>
<td></td>
</tr>
</tbody>
</table>

### XRD studies

The XRD patterns of PANI and its composites are shown in Fig. 3 and the corresponding data in Table 1. For PANI and its composites the characteristic peaks appeared in the angle range of 18.5° to 28.5°. XRD pattern of PANI with no sharp peaks indicates amorphous nature. d value decreases from PANI to other composites which reveals close arrangement of PANI chains. For PANI-PVP composite, the shifted diffraction band at 28.1° shows the incorporation of PVP into PANI matrix. PANI – PTA and PANI – PTA – PVP display broad bands at 26.3° and 28.5° respectively. For all the composite materials the average crystallite size (Scherrer method), intensities and peak positions differ from those of PANI. These observations clearly suggest that the synthesized PANI materials are amorphous in nature and have
nanoparticles [19, 21, 22]. UV-vis, FTIR and XRD studies establish that PVP and PTA are dispersed over/into the PANI matrix.

![XRD patterns of PANI materials](image)

**Fig 3.** XRD patterns of PANI materials (a) PANI (b) PANI-PVP (c) PANI-PTA and (d) PANI-PTA-PVP

### 3.4. SEM studies

The SEM images of the materials are illustrated in Fig. 4. PANI has rough-surfaced and irregularly-shaped grains of micron size (Fig. 4a). PANI-PVP composite has nano rods morphology. The rods have approximately 200 nm dia and few micron lengths. Addition of PVP into PANI as a steric regulator and template has completely changed the morphology of pristine PANI. This is in accordance with our previous works [13, 20]. However, addition of PTA to PANI has changed the PANI morphology into nano spheres (Fig. 4c). Primary nano spherical particles agglomerated into secondary clusters are visible in the image in Fig. 4c. That means the inorganic PTA is uniformly dispersed in PANI matrix and such observation was reported in previous study also [23]. The three component composite, PANI-PTA-PVP has entirely different morphology. It has somewhat fractured and irregularly shaped and sized bigger grains (Fig. 4d). This quite different morphology might have arisen by the mutual interaction between PTA and PVP, thus nullifying the steric control role of PVP.
3.5. Studies on Photodegradation

For preliminary experiment, the photocatalytic degradation of phenol was studied under conditions of 1) in light and at constant air flow, 2) in light, constant air flow and 2 ml H₂O₂ (without catalyst), 3) synthesized catalyst under dark condition and air flow. All these experiments were carried out at initial phenol concentration of 50 ppm, pH 4 and dose of catalyst of 0.5 g L⁻¹. The results of the above experiments are given in Fig. 5. In the above experiments, there was only negligible degradation of phenol. That means without catalyst or without the oxidant H₂O₂, phenol decomposition did not take place. The photocatalytic performance of the four catalysts PANI, PANI-PVP, PANI-PTA and PANI-PTA-PVP was investigated in the absence of H₂O₂ under light; [phenol]: 50 ppm; pH 4; Temp: 28±2°C; constant air flow and catalyst dose of 0.5 g L⁻¹. The results are shown in Fig. 6. The % degradation of phenol was found to be 4.5, 7.6, 9.3 and 20.7 for the four catalysts respectively. Even without H₂O₂, the catalysts are able to degrade phenol, of course, to a lesser extent. Evidently this result demonstrates that these four materials function as photocatalysts and could produce reactive oxygen species like •OH, O₂•− etc., with
aerial O\textsubscript{2} or H\textsubscript{2}O\textsubscript{2}. Also addition of PVP and/or PTA to PANI enhances the latter’s activity. Particularly, the combination PTA-PVP works better and the resulting catalyst PANI-PTA-PVP exceedingly has a higher efficiency than others. In the above experiment however, if H\textsubscript{2}O\textsubscript{2} was added, the degradation results could be far better. This is investigated in further experiments.

**Fig. 5.** Photocatalytic degradation of phenol (a) in dark in the presence of PANI and air flow (without oxidant H\textsubscript{2}O\textsubscript{2}) and (b) in light, constant air flow and 2 ml H\textsubscript{2}O\textsubscript{2} (without catalyst PANI).

**Fig. 6.** Photocatalytic performance of (a) PANI (b) PANI-PVP (c) PANI-PTA and (d) PANI-PTA-PVP in phenol degradation.
Condition: [phenol] = 50 ppm; pH = 4; Temp= 28±2°C; catalyst dose = 0.5 g L⁻¹ and constant air flow (no H₂O₂).

3.5.1. Effect of types of catalyst with H₂O₂

Fig. 7 shows the photocatalytic degradation of phenol in the presence of PANI, PANI – PVP, PANI – PTA and PANI – PTA – PVP as photocatalysts under visible light at constant air flow and 2 ml H₂O₂ addition. The degradation efficiencies of the four catalysts are 6.8, 10.0, 27.6 and 56.7% respectively at initial phenol concentration of 50 ppm, pH 4 and dose of catalyst of 0.5 g L⁻¹. On comparing the efficiency of the catalysts without and with H₂O₂ (2 ml addition to 300 ml phenol reaction solution) (Fig. 6 and 7), it is inferable that there is enhancement in efficiency with H₂O₂, particularly to a greater level for the last two catalysts PANI-PTA and PANI-PTA-PVP. Such observation is already reported [24]. Addition of external oxidant, H₂O₂ to the heterogeneous system improves the formation of hydroxyl radicals and hence the degradation extent [24]. In PANI-PTA-PVP it enhances the photodegradation by 2.5 times.

![Fig.7. Photocatalytic performance of (a) PANI (b) PANI- PVP (c) PANI-PTA and (d) PANI-PTA-PVP in phenol degradation.](image)
3.5.2. Effect of initial phenol concentration

The effect of initial phenol concentration plays a vital role for the photodegradation of phenol. The effect of initial phenol concentration at various levels of 10, 30, 50 and 70 ppm was investigated and the % degradation data are plotted in Fig. 8. Amount of degradation increases with increase in initial phenol concentration (10 ppm to 30 ppm), a maximum value is observed at 50 ppm and then it decreases at 70 ppm. Therefore 50 ppm is the optimal phenol concentration.

![Figure 8](image)

**Fig. 8.** Effect of initial phenol concentration on degradation (a) 10 ppm (b) 30 ppm (c) 50 ppm and (d) 70 ppm. Condition: pH = 4; Temp= 28±2°C; PANI-PTA-PVP= 0.5 g L⁻¹; H₂O₂= 2 ml and constant air flow.

3.5.3. Effect of pH

The effect of solution pH on the phenol removal is plotted in Figure 9. 0.1 M HCl and NaOH were used to adjust the solution at various pH values of 2, 4, 6, and 8. After 160 min reaction, the % degradation values obtained are 9.8, 56.7, 20.2 and 10.0 at pH = 2, 4, 6 and 8 respectively. The highest degradation efficiency occurred at pH = 4 and the lowest degradation at pH = 2 and 8.

The point of zero charge, pH\textsubscript{zpc} for PANI-PTA-PVP was determined as 6.91, an almost neutral pH. At highly acidic pH 2.0, the surface charge of the catalyst is positive, since H\textsuperscript{+} can be attached to aniline group. This is an unfavorable situation. While at pH 8.0, the catalyst surface may be negative. Since pKa of phenol is 11, at
higher pHs 6 and 8, the proportion of availability of phenoxide ion will be increasingly higher. Hence there could be electrostatic repulsion between phenoxide and catalyst, which renders phenol adsorption difficult. Altogether pH 4.0 is a conducive condition for maximum adsorption of phenol and is, thus the optimum pH condition. A similar observation has been noted in previous studies [25,26,27]. Thus at moderate pH value (pH = 4), phenol was degraded larger than at other pHs.

**Fig. 9.** Effect of pH variation on photodegradation of phenol (a) 2 (b) 4 (c) 6 and (d) 8.

Condition: [phenol] = 50 ppm; Temp = 28±2°C ; PANI-PTA-PVP = 0.5 g L⁻¹ ; H₂O₂ = 2 ml and constant air flow

### 3.5.4. Effect of dose of catalyst

The effect of the amount of photocatalyst on the removal of phenol is an important parameter [28] to optimize the catalyst suspension and the results are shown in Fig. 10. As expected, the increase in dose of catalyst from 0.33 to 0.5 g L⁻¹ leads to the maximum phenol decomposition of 56.7 %. Beyond 0.5 g L⁻¹ catalyst dose, the extent of phenol destruction decreases. This may be because of light scattering and screening effects [29-31]. From our findings, the catalytic loading increases the number of photons absorbed, the available active site and consequently the concentration of phenol adsorbed. At high dose light penetration is compromised because of excessive particle suspension. The trade off between these two opposing phenomena results in an optimum catalyst loading for the photocatalytic degradation.
Fig. 10. Effect of PANI-PTA-PVP catalyst dosage variation (g L\(^{-1}\)) on phenol destruction (a) 0.33, (b) 0.5, (c) 0.67 and (d) 0.83

Condition: pH = 4; [phenol] = 50 ppm ; Temp = 28±2°C ; catalyst: PANI-PTA-PVP; H\(_2\)O\(_2\)= 2 ml and constant air flow.

3.5.5. UV-Vis spectra during phenol degradation

Uv-vis spectra for photodegradation of phenol by using the catalyst PANI – PTA – PVP are shown in Fig. 11. The conditions for degradation are [phenol] = 50 ppm; Temp: 28±2°C; H\(_2\)O\(_2\) 2 ml, constant air flow and dose of catalyst of 0.5 g L\(^{-1}\). It shows that absorbance of phenol at 270 nm decreases with time. Higher catalytic activity occurred during the first 100 min of reaction and after that the catalysis occurred at a slower but constant rate and hence the pollutant disappears slowly.
Fig. 11. UV-vis spectra of phenol during its photodegradation with PANI-PTA-PVP at various time intervals of (a) 20 min (b) 40 min (c) 60 min (d) 80 min (e) 100 min (f) 120 min (g) 140 min and (h) 160 min. Condition: [phenol] = 50 ppm; Temp = 28±2°C; catalyst dose = 0.5 g L⁻¹ H₂O₂ (2 ml) and constant air flow.

4. CONCLUSION

The PANI catalysts (PANI, PANI – PVP, PANI – PTA and PANI – PTA – PVP) were prepared by chemical polymerization method. UV-vis and FTIR spectra showed the strong interaction of PTA/PVP with PANI. From SEM and XRD it is found that PANI composites are amorphous in nature but have nanostructures. Photocatalysis results showed that the highest degradation efficiency (56.7 %) occurred at pH = 4 for the medium, initial phenol concentration of 50 ppm and 0.5 g L⁻¹ of PANI – PTA – PVP, constant air flow and H₂O₂ 2 ml, under visible light. The photodegradation study suggested that the light absorption of PANI and catalytic role of PTA can be coupled nicely and thus photocatalysis functionality can be infused in PANI by doping with PTA. The soft template, PVP facilitated the role through small particle formation and active sites number enhancement. At last, it is concluded that PANI – PTA – PVP composite possesses high potential ability for photocatalytic decomposition under visible light. In conclusion, this work opens new possibilities to provide the design of new modified photocatalysts with high activity for the large-scale water treatment and other applications.
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