การบำบัดสีน้ำเสียสังเคราะห์เมลานอยดินโดยการตรึงอนุภาคนาโนซิงค์ออกไซด์เจืออะลูมิเนียมที่เป็นตัวเร่งปฏิกิริยาทางแสงด้วยบีดลูกผสมพอลิไวนิลแอลกอฮอล์–อัลจิเนต

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บทคัดย่อ

การศึกษาวิจัยครั้งนี้มีวัตถุประสงค์เพื่อศึกษาประสิทธิภาพการบำบัดสีน้ำเสียสังเคราะห์เมลานอยดินโดยบีด PVA–Alginate–Al/ZnO beads (PA–Al/ZnO beads) ที่เตรียมจากการตรึงอนุภาคนาโนซิงค์ออกไซด์เจืออะลูมิเนียม (Al/ZnO NPs) ที่สังเคราะห์ด้วยวิธีโซล–เจลอย่างง่ายบนบีดลูกผสมพอลิไวนิลแอลกอฮอล์–อัลจิเนต (PA–beads) ทดสอบประสิทธิภาพการบำบัดสีน้ำเสียสังเคราะห์เมลานอยดินที่ความเข้มข้น 100 mg/L ภายใต้การกระตุ้นด้วยแสงรวมทั้งศึกษาลักษณะสัณฐานและองค์ประกอบของบีดทั้งก่อนและหลังการทดสอบประสิทธิภาพการบำบัดสีของอนุภาคนาโนซิงค์ออกไซด์เจืออะลูมิเนียม (Al/ZnO NPs) บีดที่ไม่มีการตรึงอนุภาคนาโน (PA–beads) และเม็ดบีดที่มีการตรึงอนุภาคนาโน (PA–Al/ZnO beads) ผลการศึกษาพบว่า Al/ZnO NPs มีลักษณะโครงสร้าง 2 มิติแบบนาโนชีต โดยมีขนาดเฉลี่ยอยู่ที่ 100–500 นาโนเมตร ในขณะที่เม็ดบีด PA-Al/ZnO มีลักษณะเป็นทรงกลมสม่ำเสมอ มีค่าเฉลี่ยเส้นผ่านศูนย์กลาง 5.35±0.21 มิลลิเมตร และมีการกระจายตัวที่ดีของธาตุ Al และ Zn ในบีดชนิดนี้ เมื่อทดสอบประสิทธิภาพการบำบัดสีน้ำเสียสังเคราะห์เมลานอยดินพบว่า PA–Al/ZnO beads ให้ประสิทธิภาพในการบำบัดสีที่สูงกว่า PA–beads อยู่ที่ร้อยละ 14 ในระยะเวลา 4 ชั่วโมง ภายใต้การกระตุ้นด้วยแสง เนื่องจากการตรึง Al/ZnO NPs ช่วยเพิ่มพื้นที่ผิวสัมผัสมากขึ้น ร่วมกับปฏิกิริยาการเร่งด้วยแสงทำให้การดูดซับและการสลายสีเมลานอยดินดีขึ้น จากความสามารถในการดูดซับที่ขึ้นอยู่กับลักษณะทางโครงสร้าง ขนาด และพื้นที่ผิวดูดซับ อีกทั้งลักษณะของตัวเร่งปฏิกิริยาในปฏิกิริยาการเร่งด้วยแสง ดังนั้น PA–Al/ZnO beads จึงเป็นทางเลือกหนึ่งของวัสดุดูดซับเนื่องจากเป็นวิธีการอย่างง่ายที่มีต้นทุนต่ำ และเป็นมิตรกับสิ่งแวดล้อมที่สามารถบำบัดสีน้ำเสียสังเคราะห์เมลานอยดินได้

คำสำคัญ: พอลิไวนิลแอลกอฮอล์–อัลจิเนต บีดลูกผสม อนุภาคนาโนซิงค์ออกไซด์เจืออะลูมิเนียม ปฏิกิริยาการเร่งด้วยแสง เมลานอยดิน

Photocatalytic Decolorization of Synthetic Melanoidins Wastewater by Immobilized Al/ZnO Nanoparticles with PVA–Alginate Hybrid Beads

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Abstract

This research aimed to study the photocatalytic decolorization of synthetic melanoidins wastewater using PVA–Alginate–Al/ZnO beads (PA–Al/ZnO beads). PA–Al/ZnO beads were prepared by immobilized aluminum–doped zinc oxide nanoparticles (Al/ZnO NPs) which were synthesized by a simple sol–gel method on PVA–Alginate hybrid beads (PA–beads). Morphology, elements distribution, and the photocatalytic decolorization efficiency of 100 mg/L synthetic melanoidins wastewater by Al/ZnO NPs, PA beads, and PA–Al/ZnO beads before and after decolorization efficiency were investigated. From the results of this study, it was found that the Al/ZnO NPs exhibited the formation of 2D nanosheet structure with an average size range of 100–500 nm, whereas the PA–Al/ZnO beads exhibited a uniform spherical shape which an average diameters was 5.35±0.21 mm. and were well distributed of Al and Zn elements in this beads. The decolorized efficacy of synthetic melanoidins wastewater, PA–Al/ZnO beads showed higher efficiency than PA–beads at 14% after 4 hours under the visible light irradiation. Due to the immobilization of Al/ZnO NPs increase the adsorption area and associated with photocatalytic reactions, enhancing the efficiency of melanoid degradation. The adsorption capacity depends on the structure, size, and adsorption surface area while the photocatalysis process mainly depended on the characteristics of the Al/ZnO NPs photocatalyst. Hence, the PA–Al/ZnO NPs beads can be a promising candidate as a simple, low cost and environmentally–friendly adsorbent and suitable photocatalyst for good–performance synthetic melanoidinss wastewater treatment applications.

Keywords: PVA–alginate, Hybrid beads, Al/ZnO nanoparticles, Photocatalytic, Melanoidins

Introduction

Melanoidins is a compound resulted from Maillard reaction. Maillard reaction is commonly found in wastewater released from processed agricultural product factory especially in fermentation and distillation process (Bruhns *et al*., 2019). Due to a complex structure, dark brown color, and unpleasant smell, melanoidins become soil and water pollution. Consequently, the treatment of melanoidins via degradation and color reduction is crucial before wastewater can be release into environment (Chandra *et al*., 2008). There are various decolorization techniques for melanoidins color reduction such as adsorption (Verma *et al*., 2021), multi–oxidant system (Tripathy *et al*., 2020), bioelectrolytic (Tsiakiri *et al*., 2020) and ozonation (Mateus *et al*., 2022). However, the aforementioned techniques still have several limitations for example some techniques are expensive and produce carbon dioxide (CO_2) and volatile acids after melanoidins decolorized. The use of nanoparticles (NPs) along with immobilization technique is a promising technique that is widely used to increase decolorization efficiency. Nanoparticles are being used in this process as photocatalyst due to its high surface area. This high surface area will speed up the reaction process by using the light energy or photon to activate electrons–holes pair for oxidation–reduction process (Velan *et al*., 2015).

Zinc oxide nanoparticles (ZnO–NPs) is an extensively studied photocatalyst due to its properties such as chemically stable, cost effective, and environmentally friendly. Nonetheless, ZnO NPs has a light absorption range only at a specific range of ultraviolet radiation (UV). Due to this disadvantage, light absorption efficiency of ZnO has been improved by various techniques such as atomic structure improvement, immobilization of particle with other semiconductors, or addition of metallic and nonmetallic mixtures (Raj *et al*., 2016). From the study, aluminum (Al) is the suitable composition for light absorption efficiency of ZnO since it has low cost and environmentally friendly (Mahdavi and Talesh, 2017). According to the studies by Ahmad *et al*. (2013) and Lee *et al*. (2015), the Al/ZnO nanoparticles (Al/ZnO NPs) have revealed an efficient photocatalytic property for methyl orange degradation under visible light irradiation. However, the use of nanoparticles in the suspension form requires a post recovery method after the treatment process which is expensive and time consuming. Thus, immobilization in supported polymer absorbents is more desirable and practical which can be easily separated from the solution after treatment process. Among various polymer types, PVA is a synthetic polymer. That is resistant to both chemicals and high temperatures, inexpensive and nontoxic, and alginate is a substance extracted from seaweed. Therefore, widely used in biotechnology and wastewater treatment (Kumar *et al*., 2022). However, research and development of Al/ZnO NPs with hybrid beads (HBs) in Melanoidins treatment is still limited. By this reason, this research aimed to immobilize Al/ZnO NPs with polyvinyl alcohol (PVA) and alginate (Alg) via hybrid beads immobilization technique (PA–beads). This research also analyzes the properties of beads to be used in the treatment of synthetic melanoidins wastewater.

Objective

To study efficiency of Al/ZnO NPs with PA–beads for synthetic melanoidins wastewater treatment.

Related researches

Algarni *et al.* (2022) has studied the degradation of methylene blue (MB) and crystal violet (CV) by ZnO–80 and ZnO–180 under sunlight. The result of XRD, TEM and SEM and fluorescence spectroscopy showed that ZnO–80 NPs have smaller size than those of ZnO–180 which exhibited flakier agglomerated spherical structures. Photocatalytic activity of methylene blue by ZnO–80 was 99.64% in 45 min while ZnO–180 degraded it by 98.82% in 60 min. The higher degradation performance of ZnO–80 over ZnO–180 is due to the fact that ZnO–80 has smaller crystallites, higher specific surface area and higher pore volumes than ZnO–180.

Mahdavi and Talesh (2017) has studied about efficiency improvement of ZnO NPs by Al doping for methyl orange dye treatment via photocatalysis. ZnO NPs were synthesized by sol–gel technique with different %mol of aluminum used. From the experiment, different concentration of Al–doped yield different shapes and structures. When aluminum concentration increased, hexagonal and sphere structure transformed into rod–like structure. UV spectrum analysis result shows better degradation of methyl orange dye by ZnO doped nanoparticles under UV light and under visible light comparing to the standard particles.

Chen *et al*. (2017) has conducted an experiment to synthesize effective ZnO NPs photocatalyst by sol–gel method for azo dye degradation under UV light. The optimum condition for ZnO preparation such as clacine temperature and composite ratio on the degradation of methyl orange (MO) was investigated. In this study, the preparation of ZnO NPs at the ratio of 4 to 1 (molar ratio of oxalic acid to zinc acetate) at 400ºC exhibited the removal of methyl orange dye up to 99.70%. Moreover, the azo dye degradation rate was increased when the amount of catalyst increased and initial concentration of azo dye decreased. It can be concluded that this photocatalyst can effectively degrade azo dye. Consequently, this ZnO NPs is an efficient photocatalyst with low cost and promote environmentally friendly approach for dye treatment.

Hassan *et al*. (2014) has developed

the ZnO NPs via sol–gel synthesis. The synthesized powder of ZnO NPs was immobilized on PVA–alginate hybrid beads to separate C.I. basic blue 41 (BB 41) dye from water. The result shows that the immobilized beads presented a high strength and good chemical stability of ZnO. The immobilized beads can adsorb C.I. basic blue 41 dye up to 16.5 mg/g with initial dye concentration of 100 mg/L.

Methodology

Preparation of synthetic melanoidins

The stock of synthetic melanoidins at 1,000 mg/L was prepared by mixing 4.5 g of glucose ($C_6H_{12}O_6$, Univar), 1.88 g of glycine (NH_2CH_2COOH, Univar), and 0.42 g of sodium bicarbonate ($NaHCO_3$, Unilab) in 100 mL distilled water. Afterward, the synthetic Melanoidinss was dried in the oven at 95ºC for 7 h (Liakos and Lazaridis, 2016).

Preparation of Al/ZnO NPs

Al/ZnO NPs were prepared by a simple sol–gel method. 0.15 M of zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, Univar) was dissolved in 100 mL of methanol (CH_3OH, Merck). Then, 100 mL of 0.15 M aluminum nitrate ($Al(NO_3)_3$, Unilab) was added into solution. The mixture was stirred at room temperature for 1.5 h. Adjust the pH to 10 and stirred for another 1 h. The mixture was centrifuged (Hermle, Z 323 K) at 8,200 rpm for 20 min and washed pellet with 40% ethanol (C_2H_6O, Merck) before dried in hot air oven (Binder, ED/FD) at 105ºC and annealed in furnaces (Carbolite, CWF 11/23) at 200ºC for 2 h (Mahdavi and Talesh, 2017; Piangjai, *et al*., 2021).

Preparation of PVA–alginate hybrid beads (PA–beads)

The PA–beads were prepared by modifying the preparation technique of Hassan *et al.* (2014). 5 g of polyvinyl alcohol (PVA, Aldrich), and 0.5 g of alginate (Sigma) were dissolved in 100 mL distilled water. Then, the mixture was dropped into the mixture of 2.5 g of boric acid (H_3BO_3, Univar) and 1.5 g of calcium chloride dehydrate ($CaCl_2{\cdot}2H_2O$, Univar) in 100 mL distilled water via peristaltic pump (Shenchen pump, BT100M) at room temperature and stirred for 60 min in order to form the beads. Finally, beads were washed with distilled water before storing in distilled water for further use.

Preparation of immobilized Al/ZnO with PVA–alginate hybrid beads (PA–Al/ZnO beads)

The PA–Al/ZnO beads were prepared by modifying the preparation technique of Hassan *et al.* (2014). 5 g of polyvinyl alcohol (PVA, Aldrich), and 0.5 g of alginate (Sigma) were dissolved in 100 mL distilled water. Add 1 g of Al–doped ZnO NPs into the mixture and stirred for 2 h. Then, the mixture was dropped into the mixture of 2.5 g of boric acid (H_3BO_3, Univar) and 1.5 g of calcium chloride dehydrate ($CaCl_2{\cdot}$

$2H_2O$, Univar) in 100 mL distilled water via peristaltic pump (Shenchen pump, BT100M) at room temperature and stirred for 60 min in order to form the beads. Finally, beads were washed with distilled water before storing in distilled water for further use.

Characterization

The surface morphology and elemental distribution of Al/ZnO NPs, PA–beads, and PA–Al/ZnO beads were analyzed by using field emission scanning electron microscopy and energy–dispersive X–ray spectroscope (FE–SEM/EDX, Hitachi SU8030). Moreover, diameter and density of different bead types were measured.

Photocatalytic decolorization efficiency of synthetic melanoidins wastewater

Photocatalytic decolorization efficiency was performed by adding 10 g of each beads type into 100 mL of 100 ppm synthetic melanoidins and shacked (New Brunswick Science, Innova 2100) at 150 rpm at room temperature under the dark condition to reach the adsorption–desorption equilibrium before irradiation. The photocatalytic efficiency of beads was investigated under the 9 W visible florescence lamp with a distance of 25 cm from the lamp to the water surface. The synthetic melanoidins dye solution sample was collected at a regular interval of 30 min. The color reduction was measured at a maximum absorbance wavelength (λ_{max} = 475 nm) by the UV–visible spectrophotometer (Thermo Scientific, Genesyts 20). Then, color degradation efficiency can be calculated with the equation (1).

$$\text{Removal efficiency (\%)} = [(C_0 - C)/C_0] \times 100 \quad \text{- - - (1)}$$

where C_0 = Initial color concentration (mg/L) and C = Color concentration at different time (mg/L)

Results and discussion

Morphology of Al/ZnO NPs

The morphology of Al/ZnO NPs, PA beads, and PA–Al/ZnO beads before removal testing was investigated with FE–SEM. The Al/ZnO NPs exhibited the formation of 2D nanosheet structure with average size range of 10–500 nm (Fig. 1), which will provide low resistance to the electron transport high surface area, and beneficial for photocatalytic degradation (Piangjai *et al.*, 2021). While the PA–beads and PA–Al/ZnO beads had a uniform spherical shape and average diameters, which was 5.35±0.24 and 5.35±0.21 mm, respectively. Moreover, the PA–Al/ZnO beads, have the most complex structure, the inside surface is rough and embedded with Al/ZnO NPs (Fig. 1).

Elemental composition of Al/ZnO NPs and beads

Elemental composition of Al/ZnO NPs, PA–beads, and PA–Al/ZnO beads were conducted by EDX as shown in Fig. 2–4. The EDX mapping shows the uniform distribution of Zn

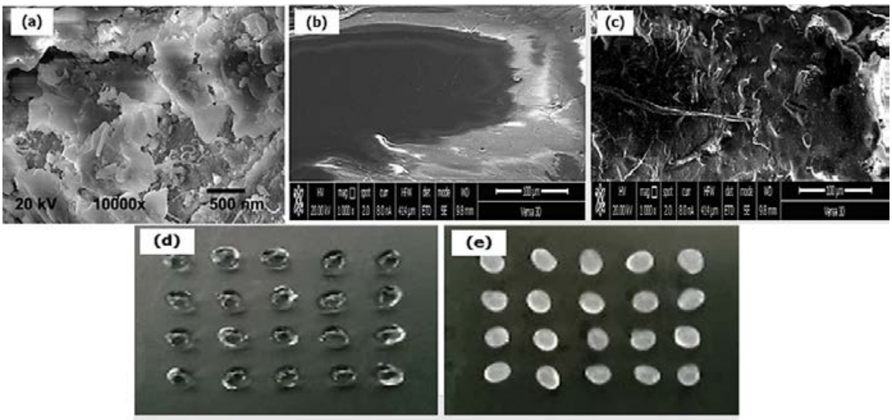

Figure 1 FE–SEM image and morphology of Al/ZnO NPs (a), PA–beads (b and d), and PA–Al/ZnO beads (c and e).

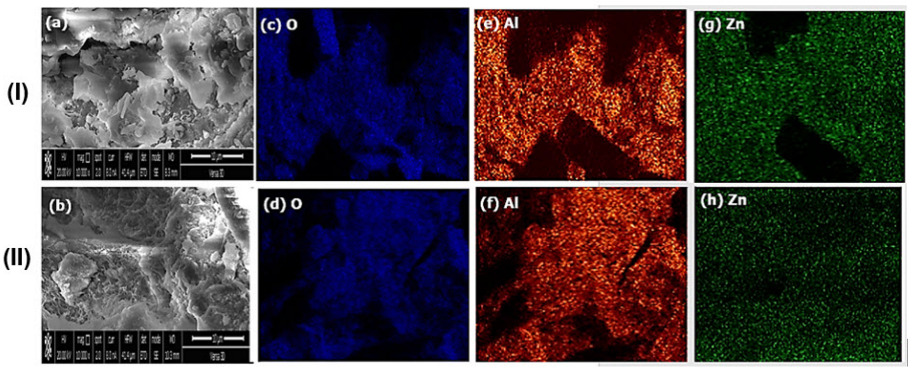

Figure 2 Morphology and elements distribution of Al/ZnO NPs before (I) and after (II) photo-catalytic decolorization of 100 mg/L synthetic melanoidins wastewater. FE–SEM (a–b) and EDX elemental distribution (c–h).

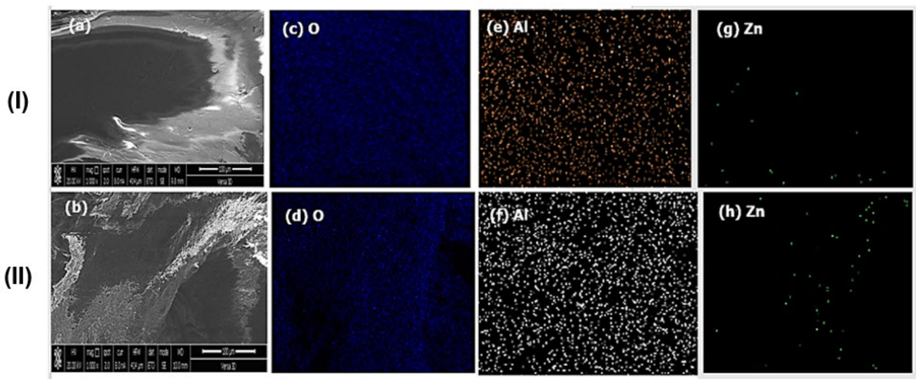

Figure 3 Morphology and elements distribution of PA–beads before (I) and after (II) photo-catalytic decolorization of 100 mg/L synthetic melanoidins wastewater. FE–SEM (a–b) and EDX elemental distribution (c–h).

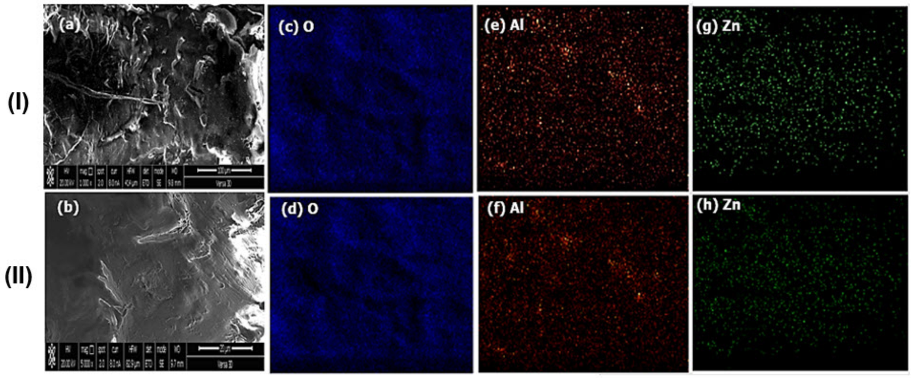

Figure 4 Morphology and elements distribution of PA-Al/ZnO beads before (I) and after (II) photocatalytic decolorization of 100 mg/L synthetic melanoidins wastewater. FE–SEM (a–b) and EDX elemental distribution (c–h).

and Al atoms in the Al/ZnO NPs and PA–Al/ZnO beads. The EDX spectra of the Al/ZnO NPs and PA–Al/ZnO beads reveal the presence of carbon (C), oxygen (O), aluminum (Al) and zinc (Zn) atoms without other impurities. Furthermore, Table 1 shows the quantitative analysis or elemental composition (wt%) of these elements before and after removal efficiency testing. This study was in agreement with Isik *et al.* (2019), a good distribution of nanoparticles in TiO_2 NPs blended beads and ZnO NPs blended beads were presented and beneficial for dye treatment application. Typically, the nanoparticles are distributed on the surface of the beads and entrapped inside the beads. However, it can be noticed that the percentage by weight of elements Al and Zn is reduced due to the coupling with PA–beads and limited detection of the FE–SEM/EDX elemental analysis technique as shown in Table 1.

Table 1 Elemental composition of samples before and after synthetic melanoidins wastewater treatment

		Composition (wt%)			
		C	**O**	**Al**	**Zn**
Al/ZnO NPs	Before dye treatment	54.73±1.99	17.27±0.81	11.17±3.03	16.83±3.83
	After dye treatment (100 mg/L)	59.13±8.41	15.96±3.23	11.64±1.17	13.27±4.50
PA-beads	Before dye treatment	53.96±0.66	45.94±0.66	0.11±0.01	0
	After dye treatment (100 mg/L)	59.40±0.70	40.60±0.80	0.1	0
PA-Al/ZnO beads	Before dye treatment	46.93±2.86	51.78±1.76	0.88±1.28	0.88±0.07
	After dye treatment (100 mg/L)	50.02±1.95	49.75±1.98	0.19±0.05	0.03±0.02

In addition, the comparison of the elemental composition of Al/ZnO NPs, PA-beads, and PA–Al/ZnO beads before and after removal efficiency testing was investigated. It was found that the increasing of carbon (C) element was found after the photocatalytic process, while the composition of Al and Zn elements was slightly decreased after testing (Table 1). This might be caused by the organic molecules of melanoidins in the synthetic wastewater were adsorbed in the beads. The analysis of the elemental composition in this study is consistent with Majidnia and Idris (2015) studies which is the study on the removal of Iodine in radioactive wastewater using maghemite and titania NPs in a photocatalytic process.

Absorption and photocatalytic degradation of synthetic melanoidins wastewater

The absorption and photocatalytic degradation efficiency of 100 mg/L synthetic melanoidins wastewater by PA–beads and PA–Al/ZnO beads was investigated. It can be obviously observed that the PA–beads and PA–Al/ZnO beads show an increase in removal efficiency and reached their maximum efficiency of 12% and 14%, respectively. This result is in accordance with the adsorption efficiency, which is both types of beads have increased adsorption efficiency as the time increased and reached maximum removal efficiency at 3.5 and 4 h of the experiment with a capacity of 120 and 145 mg/L for PA–beads and PA–Al/ZnO beads respectively. Furthermore, Al/ZnO NPs show the maximum removal efficiency at 6 hours of the experiment of 20% which is corresponding to the highest values for the absorption capacity of synthetic melanoidins wastewater at 6 hours was 20,500 mg/L. The comparison of the degradation efficiency of synthetic melanoidins wastewater showed that the Al/ZnO NPs exhibited the highest degradation efficiency of 20% Thus, Al/ZnO NPs exhibited a higher degradation efficiency than that of PA–beads and PA–Al/ZnO beads, attributing to the higher reactivity of small size with large surface area and suspended nanoparticles. Meanwhile, the PA–beads and PA–Al/ZnO beads show the degradation efficiency of 12% and 14%, respectively for synthetic melanoidins wastewater treatment (Figure 5–6).

These results demonstrated that the PA–Al/ZnO beads revealed the photocatalytic degradation efficiency of synthetic melanoidins wastewater higher than that of PA–beads under visible light irradiation. This could be attributed to a small size and high specific surface area Al/ZnO NPs, leading to improved adsorption and photocatalytic efficiency. It also suggested that Al metal can facilitate the photocatalytic activity under the visible light irradiation. This allows the limited optical catalyst to absorb only the ultraviolet spectrum to absorb more light in the visible range (Mahdavi and Talesh, 2017). This explanation is in agreement with a study of Chen *et al*. (2017), which was conducted by preparing ZnO NPs by the sol–gel method. It has revealed the high degradation efficiency (99.70%) of methyl orange dye under UV light irradiation within rapid, low cost and environmentally friendly processes. The results also showed that the degradation rate of azo dye increases with increasing catalyst amount, and reducing of the initial concentration of azo dye. It can be effectively approach in the treatment of wastewater contaminated with dyes. According to a study by Hassan *et al*. (2014), ZnO NPs were synthesized by the sol–gel method. The synthesized ZnO NPs were coupled with PVA–Alginate hybrid beads to remove azo dye (C.I. basic blue 41(BB 41)) in wastewater. It was found that the beads were strong, durable and showed absorb efficiency up to 16.5 mg/g of C.I. basic blue 41 dye at an initial dye concentration of 100 mg/L. In addition, it can be concluded that increasing the number of beads has a beneficial for the dye treatment efficiency.

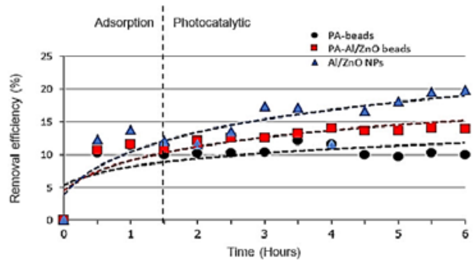

Figure 5 The photocatalytic degradation efficiency of 100 mg/L synthetic melanoidins wastewater by Al/ZnO NPs, PA–beads and PA–Al/ZnO beads

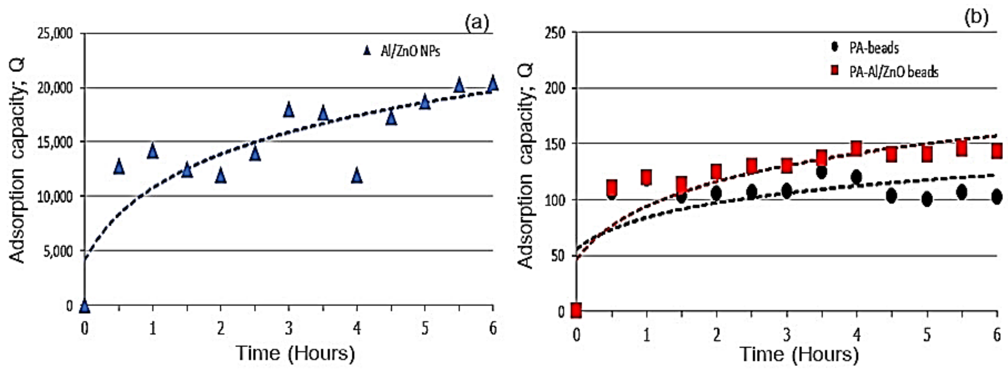

Figure 6 The adsorption capacity of Al/ZnO NPs (a), PA–beads, and PA–Al/ZnO beads (b) for 100 mg/L synthetic melanoidins wastewater treatment

Conclusions

In this study, we have successfully incorporated Al/ZnO NPs into PVA–Alg hybrid beads to greatly promote good adsorption capacity and photocatalytic activity for the degradation of high–concentration synthetic melanoidins wastewater under visible light irradiation (Table 7). The Al/ZnO nanosheet photocatalyst was synthesized by a simple and low–cost sol–gel method. The results showed the photocatalytic activity efficiency of PA–Al/ZnO beads was 14% within 4 h for removal of

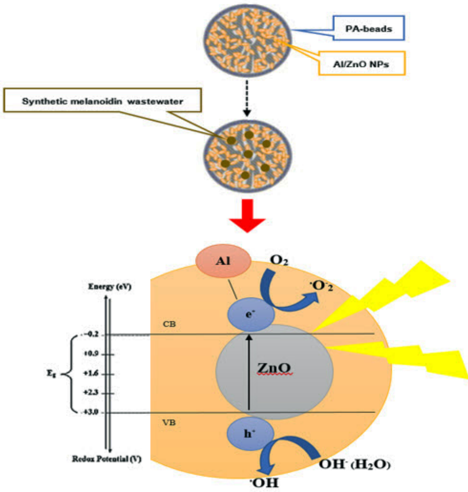

Figure 7 Photocatalytic mechanism of PA–Al/ ZnO beads for synthetic melanoidins wastewater degradation under light irradiation

100 mg/L synthetic melanoidinss wastewater. This obtained efficiency is higher than that of PA- beads, attributing to the advantage of Al/ZnO NPs coupling. It can be noted that the hybrid beads revealed a uniform spherical structure with superior properties; including a good distribution of Al and Zn elements, high adsorption capacity, and excellent photocatalytic activity under visible light irradiation. Importantly, the introduction of Al/ZnO NPs photocatalysts played a key role in increasing the adsorption property and the formation of hydroxyl groups on catalyst surfaces for photocatalytic activity. Moreover, it can be concluded that the adsorption capacity of PA–Al/ZnO beads depended on the structure, size, and adsorption surface while the photocatalysis process mainly depended on the characteristics of the Al/ ZnO NPs photocatalyst. Furthermore, the immobilization of Al/ZnO NPs into PVA–Alg hybrid beads leads to overcoming the drawbacks of Al/ZnO NPs in the suspension form which can be easily separated and recyclable after wastewater treatment process. Therefore, the synthesized hybrid beads in this study can be a promising candidate as a facile, low cost and environmentally–friendly adsorbent and suitable photocatalyst for good–performance synthetic melanoidins wastewater treatment applications. The Al/ZnO nanosheet photocatalyst was synthesized by a simple and low–cost sol–gel method. The results showed the photocatalytic activity efficiency of PA–Al/ZnO beads was 14% within 4 h for removal of 100 mg/L synthetic melanoidins wastewater.

This obtained efficiency is higher than that of PA– beads, attributing to the advantage of Al/ZnO NPs coupling. It can be noted that the hybrid beads revealed a uniform spherical structure with superior properties; including a good distribution of Al and Zn elements, high adsorption capacity, and excellent photocatalytic activity under the visible light irradiation. Importantly, the introduction of Al/ ZnO NPs photocatalyst played a key role in increasing the adsorption property and the formation of hydroxyl groups on catalyst surfaces for photocatalytic activity. Moreover, it can be concluded that the adsorption capacity of PA–Al/ZnO beads depended on the structure, size and

adsorption surface while photocatalysis process mainly depended on the characteristics of Al/ZnO NPs photocatalyst. Furthermore, the immobilization of Al/ZnO NPs into PVA–Alg hybrid beads leads to overcome the drawbacks of Al/ZnO NPs in the suspension form which can be easily separated and recyclable after wastewater treatment process. Therefore, the synthesized hybrid beads in this study can be a promising candidate as a facile, low cost and environmentally–friendly adsorbent and suitable photocatalyst for good performance synthetic melanoidins wastewater treatment applications.

In this study, the differences of beads type and synthetic Melanoidins wastewater concentration indicated significant effects on wastewater treatment efficiency. Therefore, the recommendations for further research study such as optimization the Al/ZnO NPs content in beads for other wastewater treatment, the comparison of other photocatalysts coupling with beads

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