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Synthesis of Poly(vinyl alcohol)/Chitosan/Titanium Oxide Beads

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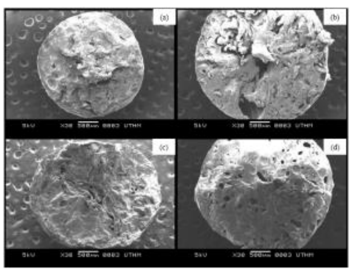
Graphical abstract



Abstract

The application of photocatalytic beads in wastewater treatment application has gained attention of many researchers. In this study, the synthesised poly(vinyl alcohol)/chitosan/Titanium oxide (PVA/CS/TiO_2) beads has been considered as a promising alternative to conventional means of wastewater treatment. The present study has successfully synthesised PVA/CS/TiO_2 beads through simple dropwise method in which varied concentration of CS from 1.0 g to 2.5 g. Morphological analysis of the synthesised PVA/CS/TiO_2 beads investigated by the FE-SEM technique revealed that porous beads were obtained regardless of the varied CS concentration content. Furthermore, solubility and swelling properties investigation of the beads were also performed within the prescribed time of 24h in three different medium which were acidic, distilled water and alkaline solution. Result of solubility test proved that PVA/CS/TiO_2 beads were insoluble only in distilled water and alkaline solution. However, the beads were found to dissolve in acidic solution due to the CS content. Meanwhile, the swelling test revealed that increased concentration of CS leads to swelling of beads in distilled water and alkaline solution. Results revealed that beads with the highest CS composition which is 2.5 g recorded 82.6% and 118.4% of swelling in distilled water and alkaline solution, respectively. In the mean time, beads with the lowest CS composition which is 1.0 g only swell for 65.8% and 93.3% in distilled water and alkaline solution, respectively. As a conclusion, the synthesised beads in this study is feasible to be applied in natural to alkaline environment.

Keywords: Photocatalytic beads; swelling; chitosan; PVA; TiO_2

1.0 INTRODUCTION

The contamination of the existing water resources is increasing day by day with industrialisation. The disposal of wastewater containing heavy metal ions is always become a challenging task for environmentalists[1]. Effective removal of heavy metal ions from aqueous solution is vital for the protection of environment and public health[2,3]. Methods such as chemical precipitation, evaporation, electrodeposition, ion exchange, adsorption, and membrane separation have been used to remove and recover metal ions from wastewater. However, these technologies are either ineffective or expensive for low concentration of heavy metals in water. Photocatalytic is one of the most effective, inexpensive, easy to operate and economical methods for the removal of heavy metals from aqueous solution[4].

Many researches and technology developers suggest that photocatalytic process offer safe, effective, efficient, durable, and affordable approach to eliminate specific types of pollutants from water[5]. It is said that photocatalysis has many advantages such as mineralisation and high degradation efficiency in treating any toxic organic materials. This technology is applied in various branches such as water purification, atmosphere purification, and antimicrobial processing[6].

As a topic of great interest, the use of poly(vinyl alcohol) (PVA) has attracted great attention in biomedical and biochemical applications about 20 years ago[7]. PVA beads have been used in the removal of lead ions from aqueous solution. PVA is water-soluble material containing large amount of hydroxyl groups [4]. It is a polymer of great interest because it offers various advantages over the conventional hydrogel, including lower cost, higher durability and chemical stability, biocompatibility, and non-toxicity to viable cells [8]. In addition, PVA is the most common material used in the immobilisation process since it is able to show elasticity and high strength [9].

However, PVA gel exhibits a high degree of swelling in water [7]. According to Zain *et al.* [4] the highly hydrophilic PVA must be crosslinked either chemically or physically to make it insoluble. By pairing the PVA with other polymer, the swelling of PVA is expected to be reduced. Chitosan is an ideal material to PVA since its availability and its ability to be made into a variety of useful forms (*i.e.* films, fibers and beads as well as powders and solutions) and its unique chemical and biological properties makes it a very attractive biomaterial for enzyme immobilization[10-12]. Chitosan (CS) is a waste by product of the shellfish processing industry and offers additional advantages of being inexpensive, plentiful, non-toxic, renewable, and biodegradable[13]. It is derived by the N-deacetylation of chitin, the major component of the shells of srustacean organisms and the second most abundant naturally occurring biopolymer next to cellulose [14]. It appears to be more useful as compared to chitin, since it has both amine and hydroxyl groups that can serve as chelating sides and can be chemically modified[15]. The presence of amine groups makes a CS unique among biopolymers, for example, its cationic in acidic solution and its affinity for heavy metal ions [16-18].

Until now, there are only few reports concerning the swelling effect of PVA/CS but not PVA/CS and other additional material. Hence, in the present study, we prepared PVA/CS/Titanium oxide (TiO_2) beads applied as photocatalyst for the removal of heavy metal ion. The solubility and swelling effect of PVA/CS/TiO_2 beads with additional CS in different quantity were further investigated.

■2.0 EXPERIMENTAL

2.1 Starting Materials

Low molecular weight of CS was purchased from Adlrich Chemistry, China. PVA was obtained from Acros Organics, New Jersey, USA. TiO_2 particles used in the present study are manufactured by QReC, Malaysia. All other chemicals were analytical reagent grade. Pure distilled water was prepared in the laboratory and was used to prepare all the solutions.

2.2 Preparation of PVA/CS/TiO_2 Beads

PVA solution was prepared by dissolving PVA in distilled water with assistance of heating at 70°C for 4h. PVA solution was then left overnight. Next, CS solution was prepared by dissolving 1.0 g CS in 2% (v/v) acetic acid solution and stirred at room temperature. Both of PVA and CS were then mixed together until resulting a homogenous solution. 0.5g of TiO_2 powders was then added into the mixture. The resulting mixture was then cross-linked in the 10 M sodium hydroxide (NaOH) solution with ethanol (95%) by drop wise method. The resulting beads were left in the cross-linking agent overnight before further treated with 0.5 M of sodium sulfate for another 30 minutes. Finally, the beads were rinsed with distilled water to remove residual agents and kept in distilled water for further use. These steps were repeated for preparing the PVA/CS/TiO_2 beads for 1.5, 2.0 and 2.5 g of CS.

2.3 Dissolution and Swelling Test of PVA/CS/TiO_2 Beads

PVA/CS/TiO_2 beads were tested with regard to their solubility in 5% (v/v) acetic acid, distilled water and 0.1 M NaOH solution by adding a known amount of PVA/CS/TiO_2 beads in each of the dilute acid, distilled water, and dilute alkaline solution for a period of 24h with stirring at room temperature.

The swelling studies of PVA/CS/TiO_2 beads were also carried out in dilute acid, distilled water and dilute alkaline solution at room temperature for a period of 24h. The swelling percentage of these beads were calculated by using the Equation 1:

$$water\ content = \frac{W_s - W}{W} \times 100 \qquad (1)$$

where W_s and W are the weight of swollen and dry beads, respectively.

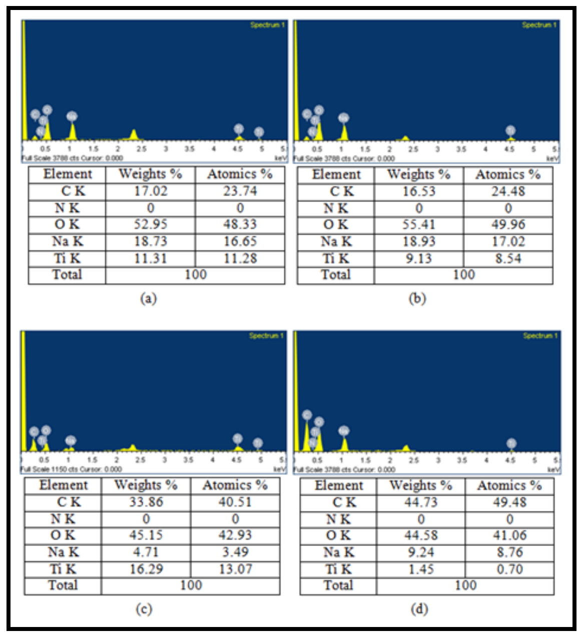
2.4 Beads Analysis

The elemental analysis of PVA/CS/TiO_2 beads surface were determined by Energy Dispersive X-ray (EDX). Beads surface morphology of the modified PVA/CS/TiO_2 beads was studied with Scanning Electron Microscope (SEM) (JOEL JSM 6380 LA, Japan).

■3.0 RESULTS AND DISCUSSION

3.1 Characterisations

EDX spectra of PVA/CS/TiO_2 beads with varied CS compositions of 1.0, 1.5, 2.0 and 2.5g are as shown in Figure 1 (a), (b), (c) and (d), respectively. It can be seen that the element of PVA, CS and TiO_2 are present in the synthesised beads. Carbon (C) element shown demonstrate that the element of PVA/CS/TiO_2 beads mainly consisted of PVA and CS. Meanwhile, titanium (Ti) element represent the TiO_2 phase for the prepared beads. However, the increament of Carbon (C) element percentages should be mainly due to the increase of CS content. Sodium (Na) element also presents in the prepared beads as a result of the cross-linking of PVA/CS/TiO_2 beads in the NaOH solution with ethanol.



(a)

Element	Weights %	Atomics %
C K	17.02	23.74
N K	0	0
O K	52.95	48.33
Na K	18.73	16.65
Ti K	11.31	11.28
Total	100	

(b)

Element	Weights %	Atomics %
C K	16.53	24.48
N K	0	0
O K	55.41	49.96
Na K	18.93	17.02
Ti K	9.13	8.54
Total	100	

(c)

Element	Weights %	Atomics %
C K	33.86	40.51
N K	0	0
O K	45.15	42.93
Na K	4.71	3.49
Ti K	16.29	13.07
Total	100	

(d)

Element	Weights %	Atomics %
C K	44.73	49.48
N K	0	0
O K	44.58	41.06
Na K	9.24	8.76
Ti K	1.45	0.70
Total	100	

Figure 1 EDS spectra of PVA/CS/TiO_2 beads with (a) 1.0g CS (b) 1.5g CS (c) 2.0 g CS and (d) 2.5g CS before the solubility and swelling test

SEM micrograph of PVA/CS/TiO_2 beads of the varied CS composition which are 1.0, 1.5, 2.0 and 2.5g are as represent in Figure 2 (a), (b), (c) and (d), respectively. Morphological analysis of the synthesised PVA/CS/TiO_2 beads investigated by the FE-SEM technique revealed that porous beads were obtained regardless of the varied CS composition applied. The porous characteristics is expected to highly contribute in reducing heavy metal ions.

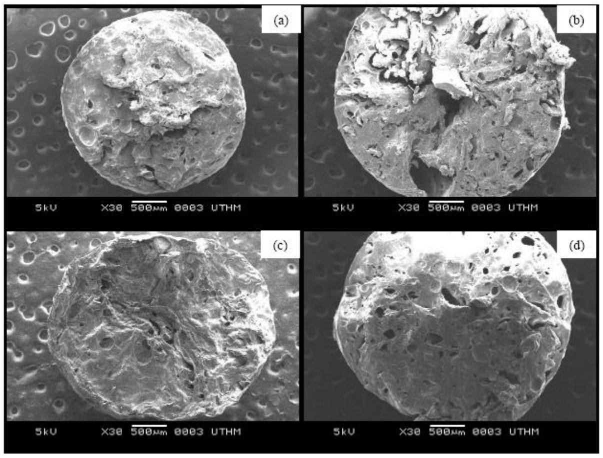


Figure 2 SEM micrograph of PVA/CS/TiO_2 beads with varied CS composition (a) 1.0g (b) 1.5 g (c) 2.0 g and (d) 2.5 g before the solubility and swelling test

3.2 Solubility and Swelling Test of PVA/CS/TiO_2 Beads

PVA/CS/TiO_2 beads with 1.0g and 1.5g of CS were found to insoluble in distilled water and 0.10 M NaOH solution but partially dissolved in the acetic acid solution (Table 1). Meanwhile, PVA/CS/TiO_2 beads with 2.0g and 2.5g of CS were fully dissolved in acetic acid solution and insoluble in distilled water and 0.10 M NaOH solution. This is due to the protonation of the amino groups found in chitosan at low pH. In an acidic solution, the polymer chains will fall apart and finally results in dissolution. Chemical modification on the beads could resolve this problem, as shown by Ngah and Fatinathan [19]. Beads dissolution either in acetic acid, distilled water and NaOH solution were observed through chemical treatment of beads. Increasing the ratio of cross-linking can actually improve the swelling effect on the adsorbent. This is due to the reaction between the primary amino groups, -NH_2 with the cross-linking agent. Thus, it reduces the number of amino groups that can be protonated which caused dissolution.

Table 1 Solubility effect of PVA/CS/TiO_2 beads of varied composition of CS applied from 1.0g to 2.5g

PVA/CS/TiO_2 beads with different composition of CS (g)	Solubility effect		
	5% (v/v) acetic acid	Distilled water	0.1 M NaOH
1.0	Partially soluble	Insoluble	Insoluble
1.5	Partially soluble	Insoluble	Insoluble
2.0	Soluble	Insoluble	Insoluble
2.5	Soluble	Insoluble	Insoluble

The water content of the polymeric beads can be related to its swelling characteristics. Generally, the beads used for adsorption column, should posses lower percentage of swelling. The percentage of swelling can be determined using the Equation 1 and shown in Table 2. The PVA/CS/TiO_2 beads showing higher percentage of swelling are not very good adsorbent and are very brittle. Based on Table 2, it can be observed that PVA/CS/TiO_2 beads with higher weight of CS shows higher percentage of swelling in distilled water and 0.1 M NaOH solution. This is because the PVA/CS beads are water loving in nature and thus have high swelling in water. Water loving nature of beads aroused due to the considerable hydrogen bonding with hydrophilic groups [20]. However, it can be seen that the PVA/CS/TiO_2 beads with 1.0g of CS used were partially soluble in acidic solution and the others were fully soluble in acidic solution. This should be due to CS nature that is soluble in even dilute organic acid solutions which is caused by the protonation of each accessible amine groups in acidic media [21]. The PVA/CS/TiO_2 beads with 1.0g of CS used were partially soluble maybe due to the least amount of CS used in this study compared to the other beads which were fully soluble in acidic solution. From Table 2, it can be concluded that PVA/CS/TiO_2 beads is soluble in acidic medium and has a higher percentage of swelling in distilled water and alkaline medium, as the concentration of CS increased.

Table 2 Swelling behavior of PVA/CS/TiO_2 beads (1.0, 1.5, 2.0 and 2.5g of CS) in different medium

PVA/CS/TiO_2 beads with different composition of CS (g)	Percentage of swelling (%)		
	5% (v/v) acetic acid	Distilled water	0.1 M NaOH
1.0	Partially soluble	65.8	93.3
1.5	Soluble	71.3	100.2
2.0	Soluble	75.1	110.7
2.5	Soluble	82.6	118.4

■4.0 CONCLUSION

PVA/CS/TiO_2 beads with different concentration of 1.0, 1.5, 2.0 and 2.5g CS were successfully synthesised through a simple dropwise method. The synthesised beads undergo swelling in natural to alkaline environment and shows complete solubility in acidic environment. Moreover, since the swelling behaviour increased with increasing CS content, it can be concluded that the CS content is in fact the determining factor of PVA/CS/TiO_2 beads solubility and swelling behaviour. The solubility and swelling behaviour was deduced to be due to the CS content in the synthesised beads.

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