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Photocatalytic removal of Reactive Red 4 dye by immobilised layer-by-layer TiO_2/cross-linked chitosan derivatives system

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ABSTRACT

The synergistic photocatalysis–adsorption processes of immobilised TiO_2/chitosan (TiO_2/CS/glass) layer-by-layer systems have been improved by the cross-linking of the chitosan (CS) sub-layer with different cross-linkers, namely epichlorohydrin (ECH) and glutaraldehyde (GLA). The immobilised layer-by-layer system was applied for the removal of an anionic Reactive Red 4 (RR4) dye solution in the presence of air and light irradiation under a 45-W compact fluorescent lamp. Based on the results, the pseudo-first-order rate constant of the TiO_2/CS-ECH/glass was more than two times faster compared to the TiO_2/CS-GLA/glass. But as the pH decreases, the TiO_2/CS-GLA system showed higher photocatalytic performance due to its better mechanical and optical properties compared to the TiO_2/CS-ECH system. In addition, the TiO_2/CS-GLA system showed excellent reusability with complete removal of the RR4 dye from the first to at least four cycles of extended usage.

Keywords: Photocatalysis; Adsorption; Titanium dioxide; Cross-linked chitosan; Layer-by-layer

1. Introduction

Dyes that discharge into the wastewater streams from various anthropogenic sources can undergo chemical changes, consume dissolved oxygen and destroy aquatic creatures [1]. Among the various methods available, conventional treatment processes such as coagulation, precipitation, biodegradation, oxidation, membrane separation, adsorption and photodegradation have been used for removing dyes from wastewater. However, due to the variability, stability and visibility of the dyes, most of the conventional treatment processes are inadequate for their effective and complete removal. A combination of two or more processes may resolve the problems.

In this context, chitosan (CS), a widely used adsorbent, has exhibited multi-functional performances with semiconductors in heterogeneous photocatalysis technologies. The CS can act as a support for the photocatalyst, enhance the adsorption-photocatalytic processes and improve the reusability of the composites. CS has been combined with various photocatalysts such as titanium dioxide (TiO_2) [2–5], zinc oxide [6], niobium oxide [7], cuprous oxide [8] and cadmium sulphide

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[9,10] for the removal of organic pollutants. But, like other polysaccharides, CS has a limitation in extreme wastewater conditions, especially in acidic mediums due to its high hydrophilicity and weak mechanical property [11]. Its slightly soluble nature, less resistant and high swelling capacities may give considerable leaching that can contribute to the increase in dissolved organic matter of the treated wastewater. Cross-linking of CS with epichlorohydrin (ECH) [12–14] and glutaraldehyde (GLA) [1,11,12,14,15] has been reported to improve the pore size distribution, mechanical resistance, chemical stability and adsorption/desorption properties [14]. It is commonly used in the form of beads [11–13], film/membrane [14,15], flakes as well as powders.

Despite that, cross-linking may reduce the adsorption capacity of the CS as the number of free active sites available for adsorption decrease due to its involvement during the cross-linking process [1,11,12] which would limit its efficiencies in the removal of organic pollutants. In addition, there is still a lack of discussion of the *in situ* immobilisation of the cross-linked CS and its application in the synergistic photocatalysis–adsorption processes in the photocatalytic degradation of coloured pollutants. Therefore, the objective of this study was to fabricate immobilised cross-linked CS derivatives, involving cross-linking with the ECH and GLA, for a simple layer-by-layer combination with the TiO_2 for the photocatalytic degradation of an anionic Reactive Red 4 (RR4) dye.

2. Materials and methods

2.1. Chemicals

The TiO_2 (99% anatase), CS flake (68.2% degree of deacetylation with a molecular weight of 322 g mol^{-1}) and RR4 with 50% dye content (Colour Index Number: 18105, chemical formula: $C_{32}H_{23}ClN_8Na_4O_{14}S_4$, MW: 995.23 g mol^{-1}, λ_{max}: 517 nm [16–18]) were purchased from Sigma–Aldrich. Phenol formaldehyde powder resin and epoxidised natural rubber (ENR_{50}) were purchased from Borden Chemical Sdn. Bhd. and Kumpulan Guthrie Sdn. Bhd., respectively. The cross-linkers namely ECH (≥98% w/v aqueous solution) and GLA (25% w/v aqueous solution) were supplied by Fluka and Merck, respectively.

2.2. Preparation of TiO_2/CS-ECH/glass and TiO_2/CS-GLA/glass

The immobilised cross-linked CS derivatives have been prepared based on previously described methods [4,12,19,20]. It basically involved four steps which are (1) CS dissolution, (2) chemical cross-linking, (3) immobilisation and (4) protonation. Each of the respective cross-linked CS derivative solutions was casted evenly on the surface of glass plates (4.7 × 6.5 cm). This fresh polymer layer was allowed to dry at room temperature (27˚C) for at least 2 d in order to produce an immobilised system. The fabricated immobilised cross-linked CS derivatives on glass plates are hereafter referred to as CS-ECH/glass and CS-GLA/glass. Fixed loading of 0.65 ± 0.08 mg cm^{-2} was used for the cross-linked CS derivatives throughout this study.

The photocatalyst formulation was prepared as described by Nawi et al. [4,21]. This TiO_2 formulation was used to immobilise the TiO_2 layer onto the CS-ECH/glass and CS-GLA/glass by a simple dip-coating method. The amount of TiO_2 coated on each respected plates is equivalent to 0.33 ± 0.08 mg cm^{-2}. The coated substrates hereafter are referred to as TiO_2/CS-ECH/glass and TiO_2/CS-GLA/glass, respectively.

2.3. Photocatalytic degradation of RR4 dye

The RR4 dye was photocatalytically degraded by the TiO_2/CS-ECH/glass and TiO_2/CS-GLA/glass systems using 30 mL of 30 mg L^{-1} dye solutions (either at pH 3.0 or 4.0). The experiments were conducted under dark and irradiated conditions using an experimental set-up as shown in Fig. 1. A 45-W Philips Ecotone fluorescent lamp with an emitted UV intensity of 6.0 W m^{-2} was used as the irradiation source. The concentrations of RR4 were monitored at 15 min intervals for a total reaction time of 2 h using a HACH DR/2000 Direct Reading Spectrophotometer at the wavelength of 517 nm. The percentage of RR4 remained (%) is defined as:

$$\text{RR4 remained} = \left(\frac{C_t}{C_o}\right)100 \quad (1)$$

where C_t and C_o are the concentration at irradiation time t (min) and the initial concentration of the RR4 (mg L^{-1}), respectively. The Langmuir–Hinshelwood kinetic model was used to determine the pseudo-first-order rate constant, and the equation is given by:

$$\ln\left(\frac{C_o}{C_t}\right) = -kt \quad (2)$$

where C_o and C_t are the initial concentration of the RR4 and the concentration at irradiation time t (min) (mg L^{-1}), respectively. The pseudo-first-order rate constant, k (min^{-1}) was calculated from the slope of the ln (C_o/C_t) vs. t plot.

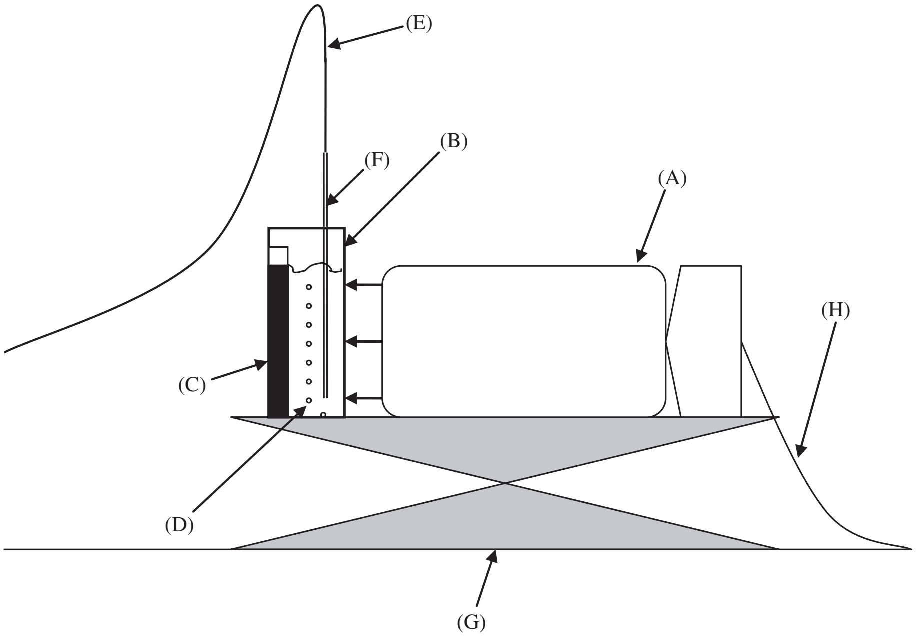

Fig. 1. Schematic diagram of experimental set-up for the irradiated condition: (A) 45-W compact fluorescent lamp with emitted UV of 6.0 W m^{-2}, (B) glass reactor cell, (C) immobilised plate (TiO_2/glass, TiO_2/CS-ECH/glass or TiO_2/CS-GLA/glass systems), (D) RR4 aqueous solution, (E) aeration supplied by an aquarium pump attached by a PVC tube, (F) pasture pipette, (G) scissor Jack and (H) power supply. The dark conditions were conducted using a similar experimental set-up, but without light irradiation.

The photocatalyst systems were recovered after each 2 h of application cycles, irradiated with a 45 W compact fluorescent lamp in ultra-pure water for 30 min and were reused again for up to four cycles to study the reusability of the TiO_2/cross-linked CS layer-by-layer systems for the photocatalytic degradation of the RR4 dye. All of the experiments were conducted in triplicates under identical conditions, and the results were reported as the average.

3. Results and discussion

3.1. Degradation of RR4 dye

The RR4 dye was employed as the model pollutant to investigate the synergistic photocatalysis–adsorption activities of the CS cross-linked derivatives in the TiO_2 layer-by-layer system under the dark and light irradiation. It is assumed that only an adsorption process would occur under the dark conditions, whereas light irradiation enables photocatalysis and adsorption processes to run concurrently. To determine the factors that influence the photocatalytic degradation of the RR4, a series of experiments were conducted using different cross-linkers (ECH and GLA) and pH (pH 3.0 and 4.0). Control experiments conducted from previous study [4,21] revealed that there was no photolysis or adsorption of the RR4 occurred in the TiO_2/glass system and that its removal under irradiation was only 11.1%.

3.2. Comparison between cross-linked CS derivatives

The different types of cross-linker used will result in different photocatalytic behaviour of the photocatalyst. Fig. 2 shows the percentage of the RR4 remaining in the sample solution by the TiO_2/CS-ECH/glass and TiO_2/CS-GLA/glass systems under dark and irradiated conditions at pH 4.0. Under dark conditions, the percentages of RR4 removed after 2 h of treatment by the TiO_2/CS-ECH/glass and TiO_2/CS-GLA/glass systems were 59.2 ± 3.1 and 26.5 ± 4.7%, respectively, whereas under the irradiated conditions, 94.1 ± 1.4 and 77.1 ± 0.1% of RR4 removal can be achieved by the TiO_2/CS-ECH/glass and TiO_2/CS-GLA/glass systems, respectively. The higher removal under the irradiated condition is mainly due to the synergistic photocatalysis–adsorption processes occurring at the same time. The synergistic effect of the photocatalysis–adsorption processes can be quantified by the R factor which can be calculated from the following equation [22]:

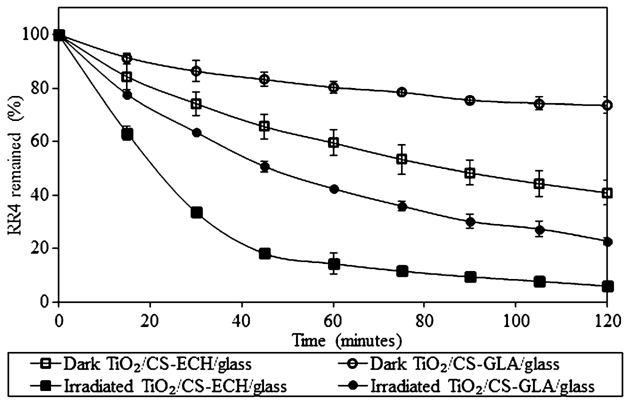

Fig. 2. Percentages of RR4 remained after the treatment by the TiO_2/CS-ECH/glass and TiO_2/CS-GLA/glass systems under dark and irradiated conditions at pH 4.0 with initial RR4 concentration of 30 mg L^{-1} and TiO_2 loading of 0.33 mg cm^{-2}.

$$R = \frac{k(\mathrm{TiO_2} + \mathrm{CS})}{k(\mathrm{TiO_2})} \tag{3}$$

where $k(TiO_2 + CS)$ is the pseudo-first-order rate constant for the TiO_2/CS layer-by-layer system, while $k(TiO_2)$ is the pseudo-first-order rate constant for TiO_2 system only. If $R > 1$, the effect is synergistic, if $R = 0$, the effect is additive, and if $R < 0$, the effect is antagonistic [23]. Based on Table 1, the effect was synergistic for all of the TiO_2/CS layer-by-layer systems, regardless the type of cross-linkers used. This shows the importance of the CS sub-layer in improving the photocatalytic process of TiO_2 photocatalyst in removing RR4 dye. The synergistic effect for cross-linked CS sub-layer is, however, less than the non-cross-linked CS as reported by Nawi et al. [4,21]. This is because the majority of $-NH_2$ and –OH groups, which are the main active groups in CS backbones, were cross-linked during the cross-linking reaction.

Table 1
Pseudo-first-order rate constant, k, and linear regression coefficients, R^2, calculated for TiO_2/glass, TiO_2/CS/glass, TiO_2/CS-ECH/glass and TiO_2/CS-GLA/glass systems

Immobilised photocatalysts	k (min^{-1})	R^2	R factor
TiO_2/glass [21]	0.002 ± 0.000	0.927	–
TiO_2/CS/glass [21]	0.064 ± 0.002	0.982	32
TiO_2/CS-ECH/glass	0.034 ± 0.008	0.983	17
TiO_2/CS-GLA/glass	0.014 ± 0.004	0.997	7

Comparing the two immobilised systems, the TiO_2/CS-ECH/glass could effectively remove RR4 better than the TiO_2/CS-GLA/glass. In fact, based on Table 1, the pseudo-first-order rate constant of the TiO_2/CS-ECH/glass was more than two times faster when compared to the TiO_2/CS-GLA/glass under light irradiation. This phenomenon is largely influenced by the adsorption behaviour of the cross-linker used. The ECH is cross-linked with CS molecules typically by connecting with the –OH groups of the CS, whereas the GLA is cross-linked mostly with the $-NH_2$ groups. Therefore, the GLA cross-linking causes a major reduction in the adsorption site ($-NH_3^+$) on the CS, thus making it significantly less effective in adsorbing RR4 dye. However, it was observed that the TiO_2/CS-GLA/glass system exhibited good photocatalytic performances, even though it possesses the poor adsorption ability. Its pseudo-first-order rate constant for the photocatalytic degradation of the RR4 under irradiation was four times faster than under dark conditions. This can be explained by its better optical properties which were proven by the PL analysis (Fig. 3). As shown in Fig. 3, the PL intensity of the TiO_2/CS layer-by-layer system decreased when the CS was cross-linked with the ECH and decreased even further when the CS was cross-linked with the GLA. This phenomenon suggested that a modification of the CS by cross-linking reactions lead to the formation of new optical properties in its cross-linked derivatives. In this case, the GLA cross-linked CS has the lowest PL intensity and thus the lower recombination rate of photoinduced electron–hole pairs. Thus, higher photocatalytic performance of the TiO_2 can be expected from its combination with CS-GLA.

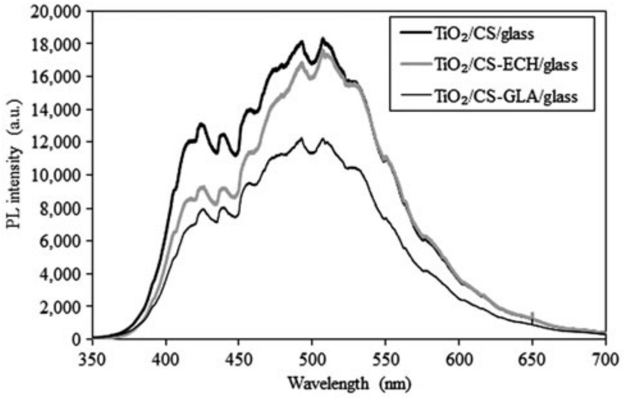

Fig. 3. PL spectra of TiO_2/CS/glass, TiO_2/CS-ECH/glass and TiO_2/CS-GLA/glass systems (excitation wavelength = 325 nm).

3.3. Effect of pH on the synergistic photocatalysis–adsorption process

The efficiency of the TiO_2/CS layer-by-layer system for the photocatalytic degradation of the RR4 is highly influenced by its adsorption towards the CS. It was reported that the adsorption of anionic dyes by the CS is pH-dependent and highly favoured acidic condition [1,24,25]. However, the CS is soluble under an acidic medium, and this could be prevented by cross-linking of the CS. Fig. 4 illustrates the reusability of the TiO_2/CS-ECH/glass and TiO_2/CS-GLA/glass systems for the photocatalytic degradation of the RR4 from the first until the fourth cycles under the dark and irradiated conditions at pH 3.0 and 4.0. The limiting pH for the TiO_2/CS-ECH/glass and TiO_2/CS-GLA/glass systems were at pH 4.0 and 3.0, respectively. This is because the CS-ECH and CS-GLA layers tend to swell below the limiting pH. The fact that the ECH could not prevent the swelling at lower pH can be explained by the availability of amino groups that can be easily dissolved due to its protonation. On the other hand, the reason that the CS-GLA layer tends to swell below the limiting pH is probably due to the presence of some free amino groups remaining in the cross-linked polymer. It was reported that 51.5% of amino groups are still available in the CS-GLA layer [20] that are accessible for dissolution and/or adsorption.

Fig. 4 shows that for the first cycle, the TiO_2/CS-ECH/glass could remove more RR4 than TiO_2/CS-GLA/glass both in dark and irradiated conditions at pH 4.0 as discussed above. However, when the pH of the solution was adjusted to pH 3.0, the photocatalytic degradation of RR4 by the TiO_2/CS-GLA/glass system was greatly improved to 71.0 ± 0.1% under dark conditions and achieved complete removal under irradiated condition (Fig. 5). This is an increase of 2.6 and 3.3 times faster than in the irradiated and dark conditions, respectively, obtained by the TiO_2/CS-GLA/glass system at pH 4.0. The high efficiencies of RR4 removed at pH 3.0 are highly depended on the adsorption of the RR4 on the CS-GLA layer which was also improved upon decreasing the pH. In fact, the pseudo-first-order rate constant of the irradiated TiO_2/CS-GLA/glass at pH 3.0 was higher than the irradiated TiO_2/CS-ECH/glass at pH 4.0 upon its reusability from the first to fourth cycles. This is because the residual amino groups of the CS in the TiO_2/CS-GLA/glass were easier protonated at a lower pH and could form an electrostatic attraction to adsorb a quantity of dye anions causing the increase in dye adsorption. The combined effects of better optical properties and better adsorption at the TiO_2/CS-GLA interface improve the electron transfer by the oxidised chemisorbed RR4 to the conduction band of the TiO_2.

However, the pseudo-first-order rate constants of the irradiated TiO_2/CS-GLA/glass system at pH 3.0 showed a slight decrease after the second cycle (Fig. 4). The decreased in the pseudo-first-order rate constants of RR4 after repeated cycles are mainly due to a reduction in adsorption efficiencies as the active sites of the adsorbent has become saturated. Even though the TiO_2/CS-GLA/glass system improved the optical properties of the photocatalyst and photocatalytic reaction at acidic pH, the pseudo-first-order rate constant was still slower than non-cross-linked

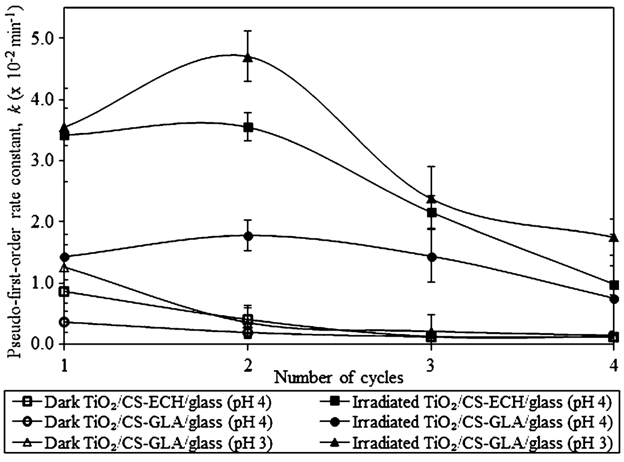

Fig. 4. Reusability of immobilised TiO_2/CS-ECH/glass and TiO_2/CS-GLA/glass systems for the removal of RR4 under dark and irradiated conditions at pH 3.0 and 4.0 with an initial RR4 concentration of 30 mg L^{-1} and TiO_2 loading of 0.33 mg cm^{-2}.

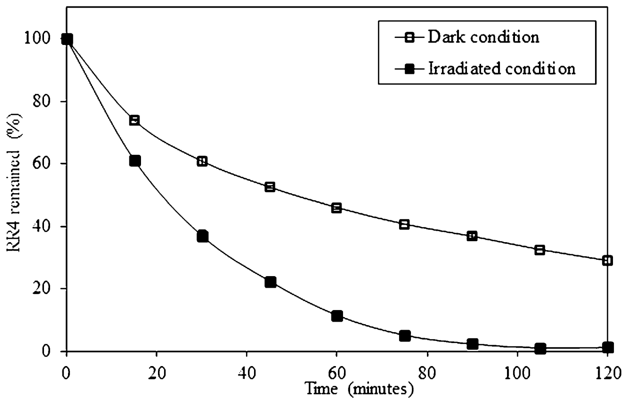

Fig. 5. Percentages of RR4 remaining after treatment by the TiO_2/CS-GLA/glass system under dark and irradiated conditions at pH 3.0 with an initial RR4 concentration of 30 mg L^{-1} and TiO_2 loading of 0.33 mg cm^{-2}.

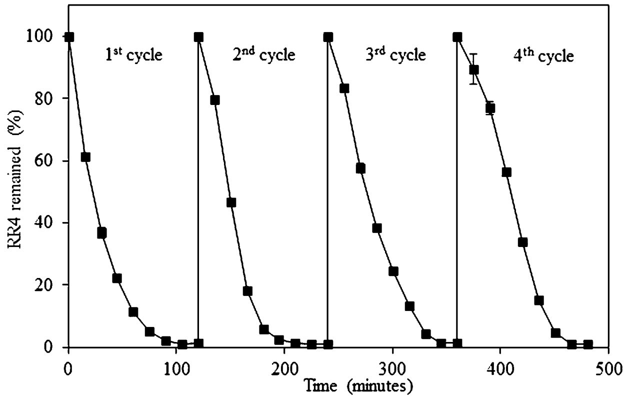

Fig. 6. Reusability of the TiO_2/CS-GLA/glass system on RR4 removal under irradiated conditions at pH 3.0 with an initial RR4 concentration of 30 mg L^{-1} and TiO_2 loading of 0.33 mg cm^{-2}.

TiO_2/CS layer-by-layer system [4,21]. This fact demonstrated that the reduction of amino groups as the main active sites in CS during the cross-linking reaction with GLA greatly reduces the synergistic photocatalysis–adsorption processes of the TiO_2/CS layer-by-layer system upon its recycled applications.

3.4. Reusability

For practical purposes, the TiO_2/CS-GLA/glass plates, after each cycle was washed for 30 min with ultrapure water and reused up to four cycles of applications in order to observe the reusability of the layer-by-layer. This is very important in order to assess the sustainability and cost effectiveness of the system. The reusability of the TiO_2/CS-GLA/glass from the first until the fourth cycles is shown in Fig. 6. Though having slower pseudo-first-order rate constants, the percentage of the RR4, removed after 2 h of treatment by the TiO_2/CS-GLA/glass system, was almost 100% even after the fourth cycle of usage.

4. Conclusion

In this study, the immobilised cross-linked CS derivatives have been successfully fabricated and adapted into a layer-by-layer combination with the TiO_2. It was found that the immobilised cross-linked CS improved the mechanical and optical properties of the immobilised TiO_2/CS layer-by-layer system. However, due to the involvement of the main active sites in the CS, namely hydroxyl and amino groups, during the cross-linking reaction, this greatly reduces the photocatalytic performance of the TiO_2/CS layer-by-layer system.

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References

[1] A.H. Chen, S.M. Chen, Biosorption of azo dyes from aqueous solution by glutaraldehyde-crosslinked chitosans, J. Hazard. Mater. 172 (2009) 1111–1121.

[2] C.E. Zubieta, P.V. Messina, C. Luengo, M. Dennehy, O. Pieroni, P.C. Schulz, Reactive dyes remotion by porous TiO_2–chitosan materials, J. Hazard. Mater. 152 (2008) 765–777.

[3] Z. Zainal, L.K. Hui, M.Z. Hussein, A.H. Abdullah, I.R. Hamadneh, Characterization of TiO_2–chitosan/glass photocatalyst for the removal of a monoazo dye via photodegradation–adsorption process, J. Hazard. Mater. 164 (2009) 138–145.

[4] M.A. Nawi, S. Sabar, A.H. Jawad, Sheilatina, W.S.W. Ngah, Adsorption of Reactive Red 4 by immobilized chitosan on glass plates: Towards the design of immobilized TiO_2–chitosan synergistic photocatalyst-adsorption bilayer system, Biochem. Eng. J. 49 (2010) 317–325.

[5] S.M. Miller, J.B. Zimmerman, Novel, bio-based, photoactive arsenic sorbent: TiO_2–impregnated chitosan bead, Water Res. 44 (2010) 5722–5729.

[6] R. Salehi, M. Arami, N.M. Mahmoodi, H. Bahrami, S. Khorramfar, Novel biocompatible composite (chitosan–zinc oxide nanoparticle): Preparation, characterization and dye adsorption properties, Colloids Surf., B 80 (2010) 86–93.

[7] J.D. Torres, E.A. Faria, J.R. SouzaDe, A.G.S. Prado, Preparation of photoactive chitosan–niobium (V) oxide composites for dye degradation, J. Photochem. Photobiol., A 182 (2006) 202–206.

[8] J.Y. Chen, P.J. Zhou, J.L. Li, Y. Wang, Studies on the photocatalytic performance of cuprous oxide/chitosan nanocomposites activated by visible light, Carbohydr. Polym. 72 (2008) 128–132.

[9] H. Zhu, R. Jiang, L. Xiao, Y. Chang, Y. Guan, X. Li, G. Zeng, Photocatalytic decolorization and degradation of Congo Red on innovative crosslinked chitosan/nano-CdS composite catalyst under visible light irradiation, J. Hazard. Mater. 169 (2009) 933–940.

[10] R. Jiang, H. Zhu, X. Li, L. Xiao, Visible light photocatalytic decolourization of C.I. Acid Red 66 by chitosan capped CdS composite nanoparticles, Chem. Eng. J. 152 (2009) 537–542.

[11] W.S.W. Ngah, S. Fatinathan, Adsorption of Cu (II) ions in aqueous solution using chitosan beads, chitosan-GLA beads and chitosan-alginate beads, Chem. Eng. J. 143 (2008) 62–72.

[12] W.S. Ngah, S. Ab Ghani, A. Kamari, Adsorption behaviour of Fe(II) and Fe(III) ions in aqueous solution on chitosan and cross-linked chitosan beads, Bioresour. Technol. 96 (2005) 443–450.

[13] W.S.W. Ngah, M.A.K.M. Hanafiah, S.S. Yong, Adsorption of humic acid from aqueous solutions on cross-linked chitosan-epichlorohydrin beads: Kinetics and isotherm studies, Colloids Surf., B 65 (2008) 18–24.

[14] P. Baroni, R.S. Vieira, E. Meneghetti, M.G.C. da Silva, M.M. Beppu, Evaluation of batch adsorption of chromium ions on natural and crosslinked chitosan membranes, J. Hazard. Mater. 152 (2008) 1155–1163.

[15] M.M. Beppu, R.S. Vieira, C.G. Aimoli, C.C. Santana, Crosslinking of chitosan membranes using glutaraldehyde: Effect on ion permeability and water absorption, J. Membr. Sci. 301 (2007) 126–130.

[16] S.W. Won, G. Wu, H. Ma, Q. Liu, Y. Yan, L. Cui, C. Liu, Y.S. Yun, Adsorption performance and mechanism in binding of Reactive Red 4 by coke waste, J. Hazard. Mater. 138 (2006) 370–377.

[17] Y.S. Al-Degs, M.I. El-Barghouthi, A.H. El-Sheikh, G.M. Walker, Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon, Dyes Pigm. 77 (2008) 16–23.

[18] T.H. Bui, M. Karkmaz, E. Puzenat, C. Guillard, J.M. Herrmann, Solar purification and potabilization of water containing dyes, Res. Chem. Intermed. 33 (2007) 421–431.

[19] A.H. Jawad, M.A. Nawi, Oxidation of crosslinked chitosan-epichlorohydrine film and its application with TiO_2 for phenol removal, Carbohydr. Polym. 90 (2012) 87–94.

[20] A.H. Jawad, M.A. Nawi, Characterizations of the photocatalytically-oxidized cross-linked chitosan-glutaraldehyde and its application as a sub-layer in the TiO_2/CS-GLA bilayer photocatalyst system, J. Polym. Environ. 20 (2012) 817–829.

[21] M.A. Nawi, S. Sabar, Sheilatina, Photocatalytic decolourisation of Reactive Red 4 dye by an immobilised TiO_2/chitosan layer by layer system, J. Colloid Interface Sci. 372 (2012) 80–87.

[22] T.T. Lim, P.S. Yap, M. Srinivasan, A.G. Fane, TiO_2/AC composites for synergistic adsorption–photocatalysis processes: Present challenges and further developments for water treatment and reclamation, Crit. Rev. Environ. Sci. Technol. 41 (2011) 1173–1230.

[23] C.G. Joseph, G.L. Puma, A. Bono, Y.H. Taufiq-Yap, D. Krishnaiah, Operating parameters and synergistic effects of combining ultrasound and ultraviolet irradiation in the degradation of 2,4,6-trichlorophenol, Desalination 276 (2011) 303–309.

[24] S. Chatterjee, S. Chatterjee, B.P. Chatterjee, A.K. Guha, Adsorptive removal of congo red, a carcinogenic textile dye by chitosan hydrobeads: Binding mechanism, equilibrium and kinetics, Colloids Surf., A 299 (2007) 146–152.

[25] M.S. Chiou, H.Y. Li, Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads, Chemosphere 50 (2003) 1095–1105.