

UNIVERSITI TEKNOLOGI MARA

**FABRICATION OF CROSS-LINKED
CHITOSAN/NANO TiO₂ HYBRID
COMPOSITE FOR REACTIVE RED
120 DYE REMOVAL FROM
AQUEOUS SOLUTION**

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ABSTRACT

In this study, cross-linked chitosan-epichlorohydrin/nano TiO₂ (CE/TiO₂) and cross-linked chitosan-glutaraldehyde/nano TiO₂ (CG/TiO₂) beads namely CE, CE/TiO₂-25, CE/TiO₂-50, CG, CG/TiO₂-25, CG/TiO₂-50 were prepared for the removal of reactive red 120 dye. Compared with the unmodified cross-linked chitosan-epichlorohydrin beads (CE) and cross-linked chitosan-glutaraldehyde beads (CG), the nano-hybrid composite beads were proved to have better sorption capacity of reactive red 120 dye (RR120), especially CE/TiO₂-50 and CG/TiO₂-25. For comparison purpose, the adsorption of RR120 by using pristine nano TiO₂ was performed as well. The composites were characterized using infrared spectroscopy, solubility test, swelling index, pH point of zero charge (pH_{PZC}), pH-potentiometric titration, CHN analysis, scanning electron microscope (SEM) analysis, and X-ray diffraction (XRD) analysis. The adsorption behavior of the unmodified cross-linked chitosan derivatives and their composites beads was compared for RR 120 uptake. Batch mode experiments were conducted as a function of the adsorbent dosage (0.02-1.40 g), pH (3-12), initial dye concentration (30-400 mg/L) and temperature (303-323K). Langmuir, Freundlich and Temkin isotherms were used to analyze the equilibrium data at different temperatures. The Langmuir gives the best fit based on the experimental data for all adsorbents. The maximum adsorption capacities of CE, CE/TiO₂-25 and CE/TiO₂-50 beads were 81.30, 135.14 and 208.33 mg/g respectively at 303 K. On the other hand, the maximum adsorption capacities of CG, CG/TiO₂-25 and CG/TiO₂-50 beads were 15.67, 44.05, 13.66 mg/g respectively at 303 K. Adsorption kinetics data were also investigated using pseudo-first order and pseudo-second order kinetics. For all unmodified and composite beads, pseudo-second order kinetics was found to describe the adsorption process better than pseudo-first order kinetics. Thermodynamic parameters such as Gibbs free energy (ΔG°), standard enthalpy (ΔH°) standard entropy (ΔS°) were evaluated by applying the Van't Hoff equation. The thermodynamics of RR120 dye adsorption onto CE, CE/TiO₂-25 and CE/TiO₂-50 beads was spontaneous and endothermic, whereas for CG, CG/TiO₂-25 and CG/TiO₂-50 beads were non-spontaneous and endothermic in nature. The chitosan/TiO₂ ratio appeared to have a significant effect on adsorption of RR120 on composite derivatives. Consequently, the adsorption capacities of CE/TiO₂-50 and CG/TiO₂-25 composite beads becomes approximately more than twice as high as their unmodified CE and CG beads, respectively, as well as pristine TiO₂ powder. The obtained results revealed the higher potential of cross-linked chitosan/TiO₂ composite beads for RR120 removal compared with unmodified cross-linked beads.

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