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Enhanced visible-light photocatalytic decontamination of methylene blue from wastewater using a biodegradable nano-composite hydrogel

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KEYWORDS

Nano-composite hydrogel, photodegradation, cationic dye, Graphene oxide, Visible light irradiation.

SHORT SUMMARY

In this study, an efficient biodegradable nano-composite hydrogel BiOCl/GO@PVA/PCMC was fabricated using natural and eco-friendly polyvinyl alcohol/carboxymethyl cellulose polymers reinforced with BiOCl/GO nano-composite, and their utility for the removal of a cationic dye, methylene blue (MB) and anionic dye, orange G (OG) was investigated. The hydrogels were synthesized using an eco-friendly technique of repeated freeze-thaw cycles. The chemical, structural, morphological, and photo-catalytic features were characterized. The coupling of graphene oxide (GO) and the BiOCl enabled the achievement of excellent photo-catalytic performance for BiOCl/GO@PVA/PCMC nano-composite hydrogel in the degradation of (MB) under visible light. The nano-composite photo-catalyst degrades MB completely within 300 min, and different photo-degradation parameters(PH of MB solution, concentration of MB solution, and doses of photo-catalyst) have been optimized by Response Surface Methodology (RSM).

EXTENDED ABSTRACT

In recent years, the synthesis and application of hydrogel have been a hot research area. In this study, an efficient biodegradable nanocomposite hydrogel BiOCl/GO@PVA/PCMC was fabricated using natural and eco-friendly polyvinyl alcohol/carboxymethyl cellulose polymers reinforced with BiOCl/GO nanocomposite, and their utility for the removal of a cationic dye, methylene blue (MB) and anionic dye, orange G (OG) was investigated. The hydrogels were synthesized using an eco-friendly technique of repeated freeze-thaw cycles. The chemical, structural, morphological, and photocatalytic features were characterized. The structure of the hydrogels was identified by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), Transmission electron microscopy (TEM), scanning electron microscopy with energy dispersive X-ray analysis (SEM–EDAX), thermalgravimetric analysis (TGA), X-ray Photoelectron Spectroscopy (XPS), Photoluminescence spectra analysis (PL), and UV–vis diffuse reflectance spectroscopy. The coupling of graphene oxide (GO) and the BiOCl enabled the achievement of excellent photocatalytic performance for BiOCl/GO@PVA/PCMC nanocomposite hydrogel in the degradation of (MB) under visible light. The nanocomposite photocatalyst degrades MB completely within 300 min under optimum conditions of (94.6%, pH 6, Dose 0.85g/L, for MB concentration 10ppm and 92%, for MB concentration 50ppm). The radical trapping studies confirmed the main active species of BiOCl/GO@PVA/PCMC during photocatalysis. Further, the BiOCl/GO@PVA/PCMC nanocomposite hydrogel remains stable under consecutive cycles.

Characterization

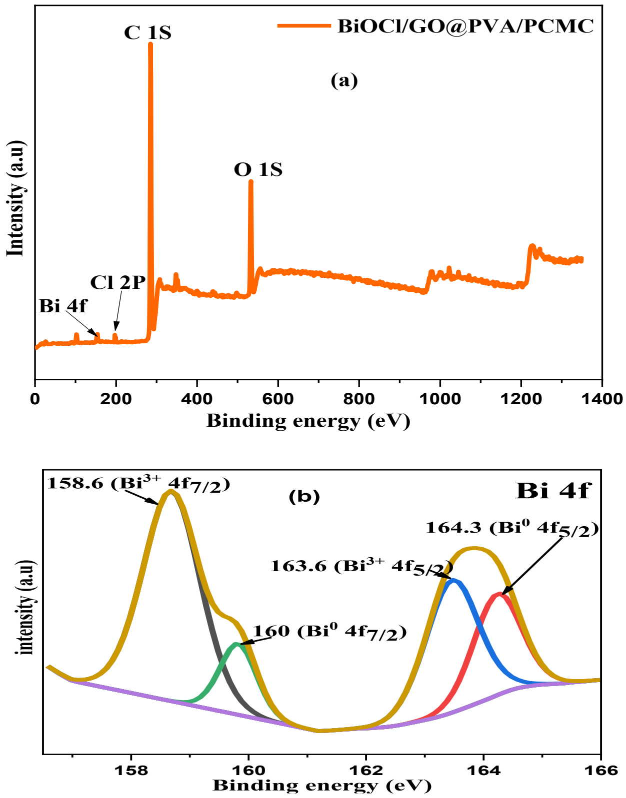
XPS

The XPS survey spectra in Fig. 1(a) show that the as-prepared photocatalyst consists of C, N, O, Cl, and Bi. On the Bi 4f core-level spectrum (Fig.1b), the two sharp peaks at 158.6 and 163.6 eV are attributed to Bi 4f $_{7/2}$ and Bi $4f_{5/2}$ signals of Bi^{3+} species, respectively. The peaks at 160.0 and 164.3 eV are characterized as Bi $4f_{7/2}$ and Bi $4f_{5/2}$ signals of metallic Bi^0 species, implying the formation of Bi nanoparticles on the surface of BiOCl nanoplates and BiOCl/GO@PVA/PCMC photocatalyst.

TEM, SEM, and EDAX

Transmission electron microscopy (TEM) analysis of GO is depicted in Fig. 2a. It is evident that GO is transparent. Figure 2b displayed the nanosheet-like morphology of the BiOCl with a size of 57.25–89.20 nm. Figure 2c demonstrated that the framework of GO in BiOCl/GO composite had a good distribution of nanosheet-like BiOCl. In SEM Fig. 2(d,e), it is clear that the nanoplates are aggregated together to form BiOCl and with adding GO, BiOCl nanoflakes BiOCl/GO composite become thinner. According to Fig.2(f,g), the morphology of PVA/PCMC hydrogels is changed after the incorporation of BiOCl/GO composite between polymeric chains in BiOCl/GO@PVA/PCMC.

It is observed that the BiOCl/GO@PVA/PCMC biodegradable composite hydrogel has a porous structure network morphology with different numbers and pore sizes as compared to PVA/PCMC hydrogel morphology. Fig. 2h shows the EDAX spectrum of BiOCl/GO@PVA/PCMC biodegradable composite hydrogel, where results demonstrate that the main elements within this sample are bismuth, oxygen, chlorine, and carbons.



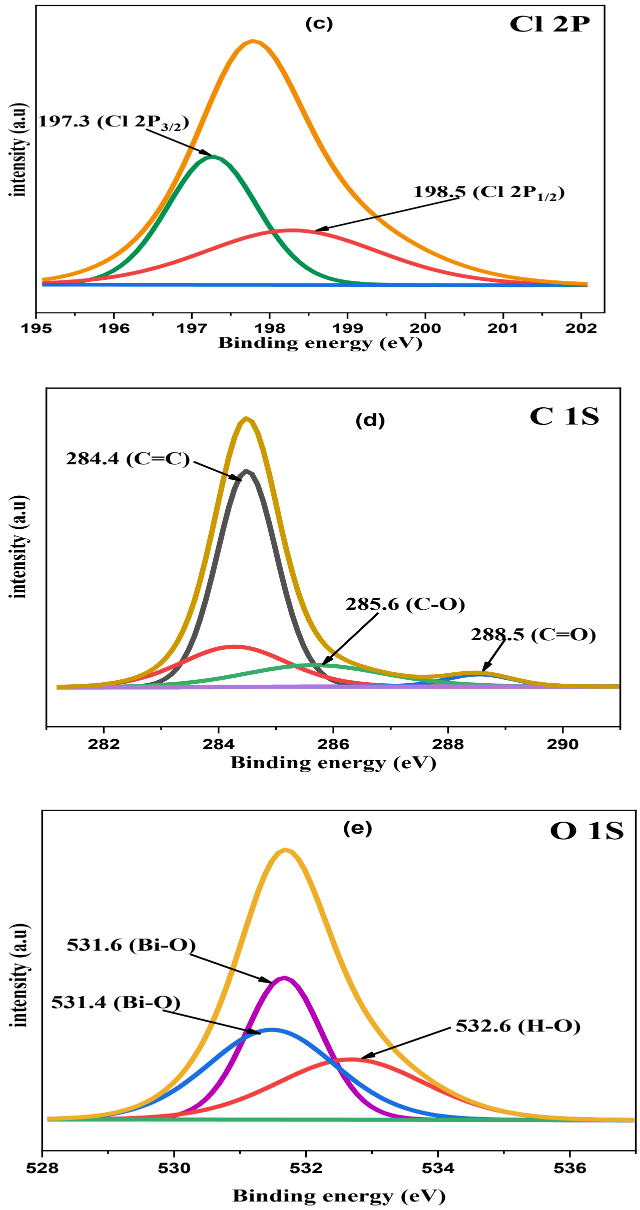


Fig.1. XPS spectrum of BiOCl/GO@PVA/PCMC biodegradable : (a) survey spectrum, (b) Bi 4f spectrum, (c) Cl 2p spectrum, (d) C ls spectrum, and (e) O 1s spectrum.

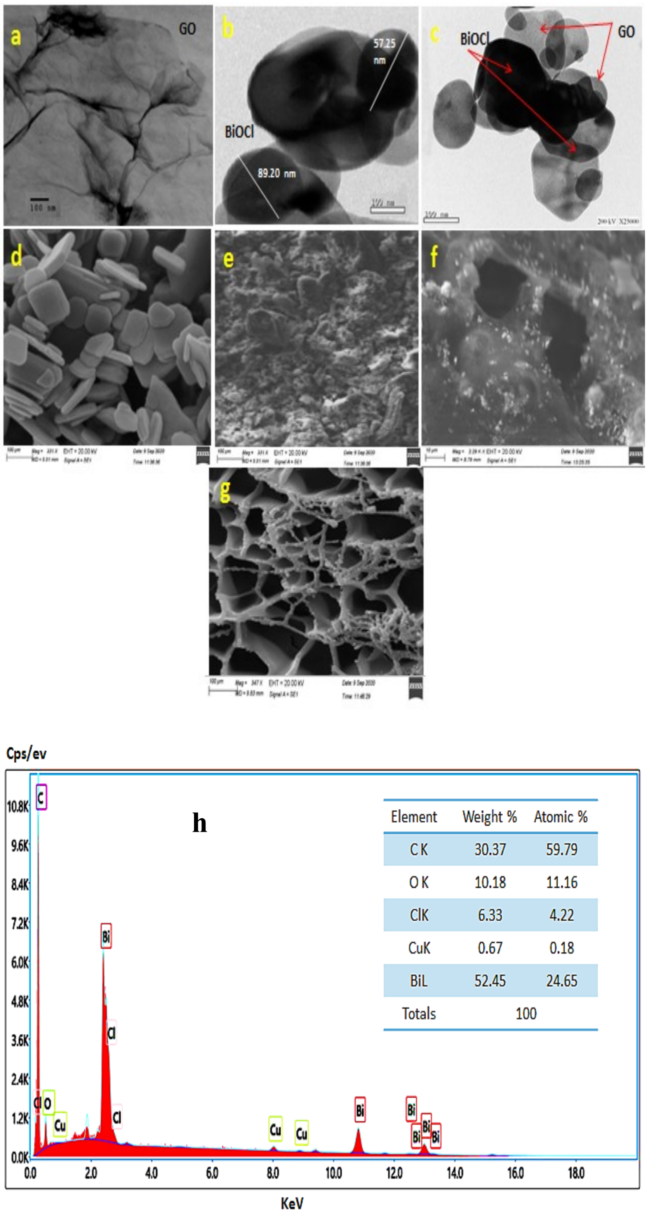


Fig.2. TEM images of as-prepared samples; (a) GO, (b) BiOCl, (c) BiOCl/GO and SEM images of the samples;(d) BiOCl, (e)BiOCl/GO, (f)PVA/PCMC, and (g) BiOCl/GO@PVA/PCMC biodegradable nanocomposite hydrogel, and EDAX spectra of; (h)BiOCl/GO@PVA/PCMC.