Functionalization of Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites using Sargassum crassifolium extract as magnetic nanophotocatalyst for cadmium sequestration

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Abstract: We report on the synthesis of Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites using Sargassum crassifolium extract as magnetic nanophotocatalyst for cadmium sequestration. Utilization of nanotechnology via surface engineering and functionalization has been considered for heavy metals sequestration. In this work, we are going to synthesize Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites via green synthesis for cadmium heavy metal sequestration on wastewater. Synthesis of nanocomposites includes the fabrication of functionalized Fe$_3$O$_4$ magnetic nanoparticles using Sargassum crassifolium extract followed by the fabrication of TiO$_2$ and finally capped with BiOCl to complete the Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites. Experimental results revealed that successful green synthesis of magnetic Fe$_3$O$_4$ via was observed in the Fast Fourier transform infrared spectra with the presence of Fe-O vibrations at 580 cm$^{-1}$. In addition, the band around 1000 cm$^{-1}$ was observed suggesting the TiO$_2$ was successfully formed the peak around 1155 cm$^{-1}$ can be attributed to Bi-Cl bond for the formation of BiOCl. Moreover, the presence of 370 nm peak in the ultraviolet-visible spectra suggests that Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites were successfully synthesized. Varied amount of cadmium on wastewater was efficiently sequestered via photocatalysis with an efficiency of about 83%. This straightforward green synthesis of Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites is a potential photocatalysts for cadmium sequestration.

1. Introduction

Gold mining has played a tremendous role in the economic development in many countries with drawback of large volume of toxic waste products which have profound impacts in the ecosystem. Proper waste management and disposal of heavy metals in mining industries can be mitigated that would result to preservation of healthy ecosystem. Most of the gold mining industries will undergo intensive mineral processing and metallurgical extraction to efficiently recover high valued minerals such as gold, nickel and copper [1]. The processing methods for minerals involve grinding of rock and ores, recovery of the desired fraction and disposal of the wastes, often as slurry, to mine tailings [2]. One such method, called leaching, is a low-cost method of removing ore from waste.
During the process, cyanide or mercury was used to dissolve gold from ores [3] and large quantities of toxic waste are produced such as cadmium which is usually present in mine tailings [4]. Thus, it is very important to have a periodic and systematic waste treatment of mine tailings to reduce the hazardous impact to the environment. There were reports that mine tailings of mining industries was able to bring environmental contaminations [5]. In fact, cadmium from mine tailing were able to contaminate drinking water [6]. Cadmium heavy metals are serious threat for living organisms, due to mutagenesis carcinogenesis and accumulation properties, even at very low concentrations [7]. The conventional mine tailings wastewater treatments include chemical precipitation, adsorption, membrane filtration, and electrodialysis [8]. The drawback in the application of these methods includes high costs, continuous input of chemicals; incomplete removal of certain metals, producing toxic sludge while the processes need high degree of operation skill. The development of innovative, cost-effective and easily engineered nanomaterials to meet the global efforts for the heavy metal sequestration has been intensively considered [9].

It has been reported that utilization of titanium dioxide (TiO$_2$) nanoparticles was utilized to excellently sequester lead and cadmium with higher efficiency [10]. However, the drawback of utilizing TiO$_2$ nanoparticles is the separation of the by-products after the wastewater treatment [11]. In addition, titanium waste is extremely acidic and its disposal methods create numerous environmental problems [12]. Moreover, zinc oxide (ZnO) nanoparticles was also utilized for cadmium wastewater treatment. High exciton binding energy of ZnO supports its activity in water purification applications. Their ability to absorb visible light and segregation of photo-excited electron/hole pair leads to surface plasmon resonance [13]. Unfortunately, toxicological studies carried out on zinc oxide nanoparticles show that potential health hazard as well as environmental risks that can have serious toxicity to bacteria, freshwater microalga, and even human cells [14].

In order to address the problem of gathering by-products after wastewater treatment, it is highly desirable to integrate magnetic nanoparticles for easy disposal of by-products using external magnet only [15]. Previous reports utilized magnetic nanoparticles such as Fe$_3$O$_4$ in wastewater treatment with remarkable efficiency [16]. In fact, Fe$_3$O$_4$ magnetic nanoparticles was synthesized using carob leaves extracts [17], Glycosmis mauritiana leaves extracts [18], Sargassum muticum extract [19], Hordeum vulgare and Rumex acetosa extracts [20], Juglans regia green husk extract [21] via green synthesis. But there are no reports on the utilization of Sargassum crassifolium which is very abundant in the Philippines and contains a potent array of antioxidants such as polyphenols, reducing sugars, nitrogenous bases, and amino acids, which is very important for reducing and stabilizing metal ions [22].

Combining TiO$_2$ nanoparticles to Fe$_3$O$_4$ magnetic nanoparticles can significantly increase the degradation efficiency of heavy metal sequestration. In fact, there were reports that utilizing Fe$_3$O$_4$/TiO$_2$ nanostructures can significantly increase heavy metal sequestration efficiency [23]. To the best of our knowledge, there are no reports that utilization of Sargassum crassifolium extract during synthesis of Fe$_3$O$_4$ magnetic nanoparticles was carried out and subsequently synthesis of TiO$_2$ nanoparticles was done to form Fe$_3$O$_4$/TiO$_2$ nanocomposites. Enhancing the photoelectrochemical performance of TiO$_2$ nanostructure, Bismuth Oxychloride (BiOCl) was added in the nanocomposites [24] to increase the sequestration activity of heavy metal. In this work, we are going to synthesize Fe$_3$O$_4$ magnetic nanoparticles using Sargassum crassifolium extract and subsequent synthesis of TiO$_2$ and BiOCl nanoparticles to form Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites for cadmium wastewater sequestration via photocatalytic reaction using ultraviolet light.

2. Experimental methods

The seaweed Sargassum crassifolium were collected in Initao, Misamis Oriental, Philippines and properly washed with deionized water and then air dried at room temperature for 5 days. The dried seaweeds were cut into small pieces and then pulverized using an analytical mill. An aqueous extract was obtained by boiling 1.0 g pulverized seaweed powder with 100 mL deionized water for 6 hours at 360 rpm. The extract solution then filtered and stored at room temperature. The core magnetic
nanoparticles were prepared using 2.16 g of FeCl$_2$•6H$_2$O dissolved in 200 mL deionized water and 0.4 g of FeCl$_3$•4H$_2$O dissolved in 100 mL deionized water. A 10 mL of seaweed extract was then added to the 100 mL iron salt solution while continuously stirred at 360 rpm for 15 minutes. Dropwise addition of NaOH solution was done to maintain at pH 11. The resulting magnetic nanoparticles (MNP) precipitate was washed with deionized water.

For the synthesis of MNP@TiO$_2$ nanocomposite, 2 mL of titanium butoxide was added to the 20 mL isopropanol in a 250 mL beaker and followed by the addition of distilled water and isopropanol while stirred at 360 rpm. The resulting nanocomposites were washed with isopropanol and subsequently dried in vacuum. The Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites were prepared through a precipitation process at a room temperature. Bi(NO$_3$)$_3$·5H$_2$O was dissolved in 20 mL of 4M HNO$_3$ aqueous solution and mixed with NaCl and Fe$_3$O$_4$/TiO$_2$ nanocomposites while stirring until precipitate was observed. The precipitate was separated and washed using isopropanol and distilled water and subsequently dried. The Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites were characterized using Fast Fourier transform infrared spectroscopy (FTIR) to determine the vibrational mode. Ultraviolet-Visible (UV-Vis) spectroscopy was done to determine the optical property of the synthesized nanocomposites. The photocatalytic activity of the prepared nanocomposites for cadmium sequestration under UV light irradiation was investigated by varying amount of cadmium using the synthesized Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites.

A diluted cadmium solution was prepared to desired concentrations such as 2.5, 5.0, 15.0, 30.0 and 50.0 ppm while maintaining at pH 6.0. The actual initial concentration of cadmium was measured using an ion selective electrode (ISE) meter and recorded. A 50.0 mg of Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites used as the nanophotocatalyst. These nanocomposites were added to a 50 mL of different diluted cadmium solutions for photocatalytic degradation activity. The mixture solution was irradiated with ultraviolet light for 40 min and measured the amount of remaining cadmium using ISE meter every after irradiation.

3. Results and discussion
The FTIR spectra of the synthesized Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites using varied amount of Sargassum crassifolium extract is shown in figure 1. For comparison, the FTIR spectra for seaweed extract, Fe$_3$O$_4$ and Fe3O4/TiO$_2$ nanocomposite are also included. It is observed the presence of characteristic peak at around 580 cm$^{-1}$ correspond to Fe-O bending suggesting the formation of core Fe$_3$O$_4$ magnetic nanoparticles. This is due to the stretching vibration bands related to the metal in the octahedral and tetrahedral sites of the oxide structure. Obviously, this peak is absent for the Sargassum crassifolium extract only. On the other hand, vibrational peak at around 3300 cm$^{-1}$ for seaweed extract indicates the presence of O-H bonds while vibrational mode at 1610 cm$^{-1}$ is attributed to the conjugated carbonyl (−C=O) group [25]. In addition, TiO$_2$ nanoparticles was successfully formed due to the presence of the intense broad band below 1000 cm$^{-1}$ corresponds to Ti-O-Ti vibrations which imply to the formation of TiO$_2$ layer [26]. Likewise, the peak at 1458 cm$^{-1}$ indicates the presence of Bi-Cl bonds.

Figure 2 shows the UV-Vis spectra of Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites. It is observed that the peaks from 320 to 350 nm can be attributed to the local vacancies present in the Fe$_3$O$_4$ nanoparticles due to surface plasmon resonance of electrons of metal which consists of a collective oscillation of conduction electrons excited by the incident light. The peak around 354 to 357 nm can be attributed to TiO$_2$ while peaks around 360-380 nm is attributed to the formation of pure BiOCl.

The transmission electron micrograph of synthesized Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites is shown in figure 3. It is observed the presence of nanoparticles with an average size of 15 nm. Moreover, aggregated nanoparticles are seen in the TEM image. This is a manifestation that we successfully synthesized Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites. The TEM measurements of Fe$_3$O$_4$ and Fe$_3$O$_4$/TiO$_2$ nanoparticles are underway to compare the morphology and particles size and will be reported elsewhere.
Cadmium sequestration was tested using Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites with varying amount of cadmium concentrations as shown in figure 4 in the presence of ultraviolet light. It is very apparent that about 83.48% of cadmium has been sequestered using the Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites. Moreover, the sequestration efficiency of cadmium in wastewater decreases as the amount of cadmium increases. This might be due to the saturation of sequestration capability of Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites. It is also observed that as the amount of cadmium in wastewater reaches to 50.0 ppm, the sequestration efficiency drastically drops below 50%. This might be due to the lower amount of Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites added in the treated cadmium wastewater. It is suggested that there must be a balance between the amount of Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites and the amount of cadmium concentration in wastewater treatment.
4. Conclusions
The magnetic Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposite was successfully synthesized via green synthesis route using Sargassum crassifolium extract through a precipitation process. FTIR and UV-Vis spectra revealed that successfully formation of Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites and confirmed in the TEM micrograph. Higher efficiency of cadmium sequestration was done and found out that there must be a balance between the amount of Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites and cadmium concentration. It is highly recommended that optimization must be done in order to obtain higher cadmium sequestration efficiency. Likewise, XRD measurement is highly recommended to for Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites to determine its magnetic phase.

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Figure 4. Cadmium sequestration efficiency of Fe$_3$O$_4$/TiO$_2$/BiOCl nanocomposites with varying cadmium concentrations.
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