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Adsorption and Photocatalytic Study of Integrated Photocatalyst Adsorbent (IPCA) using $LaFeO_3$-GO Nanocomposites for Removal of Synthetic Dyes

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In this research, Lanthanum Orthoferrite-Graphene Oxide ($LaFeO_3$-GO) IPCA nanocomposites were synthesised via sol-gel glucose method. Fourier Transform Infrared Spectroscopy (FTIR), Autopore Porosimeter and UV-Vis Spectrophotometer measurement were used for the characterisation of the nanocomposites. The effect of certain ratios of GO deposited on $LaFeO_3$ were investigated for removal of methylene blue and methyl orange dyes through adsorption-photocatalytic activity. Among all samples, excellent removal of methylene blue could be observed in 5 % GO in $LaFeO_3$-GO IPCA nanocomposites that demonstrated 100 % degradation efficiency within 60 min under visible light irradiation. For adsorption under dark condition, 2 % GO in $LaFeO_3$-GO nanocomposites achieved 98 % removal of methyl orange within 2 h. It could be concluded that synergetic effect between photocatalysis and adsorption can give significant impact for removal of synthetic dyes from aqueous solution.

1. Introduction

Textile industry is one of largest industry that contributes to the growth of economic nation. The significance growth from textile industry showed dyes are produced each year throughout worldwide ranging from 700,000 to 1,000,000 t. Synthetic dyes are common for industrial textile company to produce in large scale compare to natural dyes. It is because synthetic dyes offered less cost production, ability to portray broad range of colour, and perform better from its fastness specification (Sattler, 2010). High discharged of synthetic dyes into environment without proper wastewater treatment can cause serious water pollution as the effluents contain toxic organic chemicals and heavy metal ions (Ibrahim et al., 2010). Conventional methods including membrane filtration, microbiological or enzymatic, adsorption, photocatalyst, etc. are proposed by researchers to remove synthetic dyes effectively (Shah et al., 2013). Amongst these, photocatalyst is seen as improved technology that has a bright potential for wastewater treatment applications.

Lanthanum orthoferrite ($LaFeO_3$) is one of the promising photocatalyst exist from perovskite material. Its special properties consists of high stability, non-toxicity and small band gap energy (2.07 eV), made this type of perovskite an interesting visible light active photocatalyst (Iervolino et al., 2016). Individual act by $LaFeO_3$ was not much improved from its photocatalytic performance. This is because the nanoparticles of $LaFeO_3$ were susceptible to agglomeration due to its high surface energy. By scattering the nanoparticles onto a support material, it is an effective way to treat the agglomeration of the nanoparticles and the support material provided heterojunction for electron and holes that limit the charge recombination (Vaiano et al., 2017).

There had been many support materials uses to support the nanoparticles and show excellent performance enhancements due to high specific surface area and dispersion capacity (Peng et al., 2016). Graphene oxide (GO) had attracted huge attention due to its characteristics for adsorption application including large surface area, mechanical stability, tuneable electrical and optical properties (Li et al., 2015). GO molecular plane acquired many oxygen functionalities which could be produced in large quantities and dispersed in various

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solvents. Studies currently had outlined that the GO supported photocatalyst produced excellent photocatalytic performance mainly due to the enhancement in adsorption rate of pollutant and light absorptivity of the composite. Since nanoparticle $LaFeO_3$ had been proven to be effective in the degradation of dye water, GO supported $LaFeO_3$ can be possibly applied with the synergistic advantage of visible light photocatalysis and adsorption.

In this particular study, the effects of GO ratios on $LaFeO_3$ nanocomposites material were investigated. The adsorption and photocatalytic activities were tested on methylene blue and methyl orange dyes. Later, all the prepared samples were characterised using Fourier Transform Infrared Spectroscopy (FTIR) to observe the presence of functional groups in the $LaFeO_3$-GO nanocomposite and Autopore Porosimeter to measure its total surface areas.

2. Materials and Methods

2.1 Materials and Reagents

Lanthanum (III) nitrate hexahydrate, $La(NO_3)_3.6H_2O$ and glucose were purchased from Merck Co Ltd. Iron (III) nitrate nonahydrate, $Fe(NO_3)_3.9H_2O$ and graphene oxide, GO is purchased from Sigma-Aldrich Ltd. For targeted pollutants, methylene blue (MB) and methyl orange (MO) were employed to test the photocatalytic activity under visible light irradiance using LED (100 W) light source (Phoenix Electric Co., Ltd. Himeji Japan).

2.2 Synthesis of Lanthanum Orthoferrite ($LaFeO_3$)

The preparation of $LaFeO_3$ powders was carried out according to sol-gel glucose method. Equimolar amounts of lanthanum nitrate hexahydrate ($La(NO_3)_3.6H_20$) and iron (III) nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$) were added into 80 % glucose solution pre-heated to 60 °C. The molar ratio of glucose to metal ions (glucose/M) were 3 : 10. As both salts were completely dissolved in the glucose solution, the temperature was raised to 70 °C to evaporate excess water and subsequently increased the mixture's viscosity. A gel was formed with the release of violent NO_x gas resulting from the decomposition of nitrate ions. The resultant gel was then heated in an oven at 250 °C for 2 h. The resulting specimen was ground into fine powder to obtain $LaFeO_3$ precursor. Then, the precursor is calcined at 500 °C for 2 h to obtain the final product, which are $LaFeO_3$ powders.

2.3 Preparation of $LaFeO_3$-GO IPCA Nanocomposite

The preparation of $LaFeO_3$-GO IPCA nanocomposite in this experiment was accordance to previous study (Vadivel et al., 2014). Initially, GO was suspended in 25 mL deionised water under vigorous stirring using magnetic stirrer. The initial weight of GO was measured at 2 % from the total weight of the desired nanocomposite. Table 1 shows the preparation of IPCA and their respective specific surface area (SSA).

Table 1: Preparation of IPCA and their respective specific surface area (SSA)

Sample	Graphene Oxide (GO)	Lanthanum Orthoferrite ($LaFeO_3$)	Specific surface area (m^2/g)
0 % IPCA	0 %	100 %	3.89
2 % IPCA	2 %	98 %	17.36
3 % IPCA	3 %	97 %	16.94
5 % IPCA	5 %	95 %	20.31

The measured amount of LaFeO3 was then dissolved in 25 mL of deionised water. Both mixture consisted of $LaFeO_3$ and GO were simultaneously mixed using sonicator for 2.5 h and later mixed again using magnetic stirrer for 6 h in room temperature in order to form a homogenous solution. The solution was then filtered using ethanol, and dry at 40 °C for 8 h to obtain the $LaFeO_3$-GO IPCA nanocomposite. Procedures were repeated to prepare different ratio of $LaFeO_3$-GO IPCA nanocomposite (see Table 1).

2.4 Characterisation

The IPCA nanocomposites' functional groups were analysed and identified using model 6300 FTIR spectrometer. Specific surface area of IPCA samples were measured using Micromeritics MicroActive AutoPore V 9600 Version 1.03 by applying mercury porosimetry analysis technique.

2.5 Photocatalytic and Adsorption Test

In this work, photocatalytic activities of $LaFeO_3$-GO composites were tested on MB and MO dyes. The photocatalytic activities were carried out using LED light (100 W) to emulate the visible light condition. The arrangement for the photocatalytic activity as follows: distance between the samples and the source fixed at

10 cm. 100 mL of MB and MO dyes with the initial concentration fixed at 13 mg/L were poured into 500 mL beaker. 0.1 g of $LaFeO_3$-GO IPCA nanocomposites were weighed and added into the targeted pollutants. Prior to photodegradation study, $LaFeO_3$-GO composites were allowed to reach adsorption-desorption equilibrium for at least in 120 min by continuous stirring, followed by irradiation of visible light for 120 min. As the photocatalysis took place, 5 mL aliquots were taken every 20 min and filtered to separate $LaFeO_3$-GO composites. Concentration of MB and MO were monitored by measuring the absorbance value of samples using UV-Vis Spectrophotometer (HACH Model DR5000) at λ = 644 nm and λ = 465 nm.
Adsorption properties of neat GO and $LaFeO_3$ for methylene blue and methyl orange dyes were evaluated by stirring a mixture of methylene blue or methyl orange dye in dark condition for 1 h with specified amounts of GO and $LaFeO_3$. Later, 10 mL aliquots were taken at every 10 min and analysed using UV-Vis spectrophotometer to evaluate adsorption capacity. Wavelengths for adsorption rate measurement of methylene blue and methyl orange dyes was fixed at λ = 644 nm and λ = 465 nm. The photocatalytic activity and adsorption performance for MB and MO dyes removal were calculated and evaluated using Eq(1):

$$\text{Removal of dyes (\%)} = \frac{C_o - C_t}{C_o} \text{ x } 100\ \% \quad (1)$$

Where C_o (mg/L) is the initial concentration of dyes, C_t (mg/L) is the final dyes concentration.

3. Results and Discussions

3.1 FTIR Spectroscopy

FTIR analysis was carried out in order to understand the interface characteristics of the IPCA nanocomposites. The FTIR spectra clearly showed the vibrational bands of 2 %, 3 % and 5 % IPCA in Figure 1. Basically, the vibrational pattern of the fabricated IPCA showed higher resemblance towards the $LaFeO_3$ vibrational pattern, which probably due to the higher amount of $LaFeO_3$ used in the composite. For 5 % IPCA, the characteristic band at 426.59 cm^{-1} corresponds to the Fe-O stretching vibrations which were attributed by the octahedral FeO_6 group in the perovskite compounds (Peng et al., 2016). The band at 3,399.63 cm^{-1} was attributed to the O-H in absorbed water and hydroxyl groups. The bands at 1,634.94 cm^{-1} and 1,479.21 cm^{-1} were attributed to the splitting of asymmetric stretching of carbonates that indicates La-carbonate species were formed on the surface of the perovskite due to the exposure to the surrounding atmosphere (Thirumalairajan et al., 2012). The surface of the $LaFeO_3$ was prone to chemisorption of CO_2 gases in ambient which led to the formation of carbonate ions. The band at 873.71 cm^{-1} was due to carbonates (Cho et al., 2009). In the vibration band of 3 % IPCA, broad peak at 3,388.10 cm^{-1} represented the O-H stretching, 1,496.28 cm^{-1} corresponded to carbonyl stretching, 1,204.80 cm^{-1} attributed to C-O-C stretching vibrations (Vadivel et al., 2014). At 1,419.22 cm^{-1} peak was due to the presence of absorbed water and the skeletal oxidation of unoxidised graphite (Yang et al., 2012). In the FTIR spectra of the IPCA composite, it was reported that some of the peaks had shifted to lower frequency such as 3,399.63 cm^{-1} to 3,388.10 cm^{-1} (O-H), 1,501.94 cm^{-1} 1,479.21 to cm^{-1} (carbonates) and 559.54 cm^{-1} to 555.02 cm^{-1} (Fe-O). This was most probably due to strong interaction between the lanthanum orthoferrite ($LaFeO_3$) and graphene oxide (GO) matrix in the IPCA (Zhu et al., 2011). The FTIR spectrum had suggested that the $LaFeO_3$ photocatalyst has successfully embedded at the surface of the GO sheets.

3.2 Surface Area Measurements

Specific surface area (SSA) of composites also gave impact to the performance in MB and MO removal (Aziz and Ismail, 2015). As shown in Table 1, the specific surface area (SSA) of $LaFeO_3$-GO nanocomposites showed a slight increase from 17.359 up to 20.307 (m^2/g) by increasing the ratio of GO deposited on $LaFeO_3$. Meanwhile for pristine $LaFeO_3$, the SSA showed only 3.89 (m^2/g). It is important that adsorption can portrayed good efficiency for removal dyes if SSA is high (Ndi Nsami and Mbadcam, 2013).

3.3 Adsorption and Photocatalytic Studies of $LaFeO_3$-GO Nanocomposite

In this research, GO is selected as the adsorbent to be integrated with $LaFeO_3$. Previous research stated that GO is known as powerful material in adsorption which required investigation of individual performance of both bare materials, $LaFeO_3$ and GO (Wang et al., 2014). Besides, adsorption was also known to be an integral part of heterogeneous photocatalysis. Adsorption capacity of MB and MO for neat $LaFeO_3$ and GO are shown Figure 2. The adsorption of both dyes, MB and MO were dominantly ruled by GO while $LaFeO_3$ showed weak performance in adsorption process.

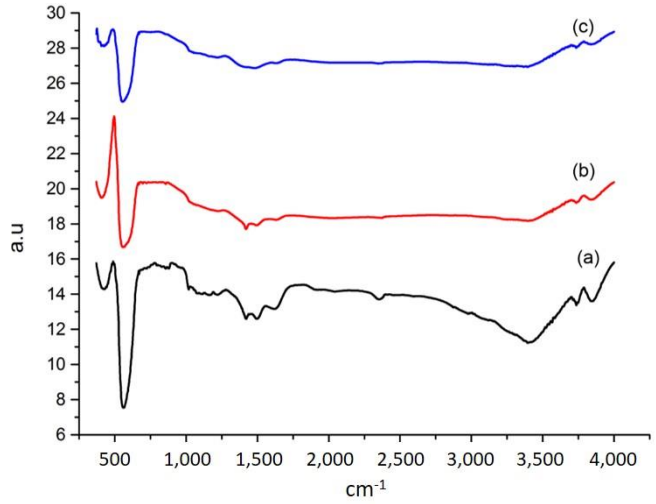

Figure 1: FTIR spectrum of $LaFeO_3$-GO composites by different ratios (a) 2 % (b) 3 % (c) 5 %

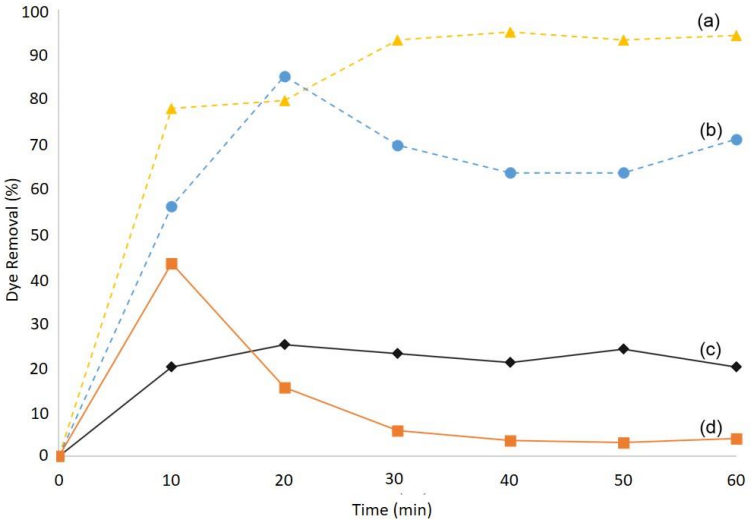

Figure 2: Dye removal performance of GO (dotted line) and $LaFeO_3$ (line). (a) and (c) marked the removal of methylene blue dye, and (b) and (d) marked the removal of methyl orange dye

Next, the investigations are continued by applying $LaFeO_3$-GO composites in dark condition (adsorption) coupled with photocatalysis under visible light irradiation. In which, the amount of GO ratios were varied at 2 %, 3 % and 5 % pH 7 condition. As portrayed in Figure 3, the increased ratio of GO until 5 % lead to increasing adsorption efficiency of MB dye up until 91 % in 120 min (Mutalib et al., 2018). For MO removal, by lowering the ratio of GO to 2 % increased the adsorption efficiency up until 98 % in 120 min. This phenomenon can be mainly related to the structure of ionic configuration and structures of the dyes with composites. MO is an anionic compound with a reactive SO^{3-} group reacted with cationic elements. While former structural models of GO indicated that it composed of graphene-like sheets with oxygen (O^{2-}) groups which also anionic. This can give repulsion force for both GO and MO to react. With the combination of GO and $LaFeO_3$, cation from $LaFeO_3$ (La^{3+}, Fe^{2+}) can gave higher adsorptive ability with the help from adsorbent ability of GO created larger surface area for adsorption (Peng et al., 2016). Hence, high amount of $LaFeO_3$ content in $LaFeO_3$-GO composites caused higher adsorption rate of MO. Another reason to explain the better adsorption rate of $LaFeO_3$-GO composites for MO compared to MB is when comparing the ionic structure of them with composite GO and $LaFeO_3$, two attraction forces (cation; La^{3+}, Fe^{2+}) reacted with anionic MO will create higher adsorption rate compared to one attraction force (anion: O^{2-}) reacted with cationic MB dye with $C–S^{+}=C$ functional group attracted only to elements of anionic (Trandafilovic et al., 2017).

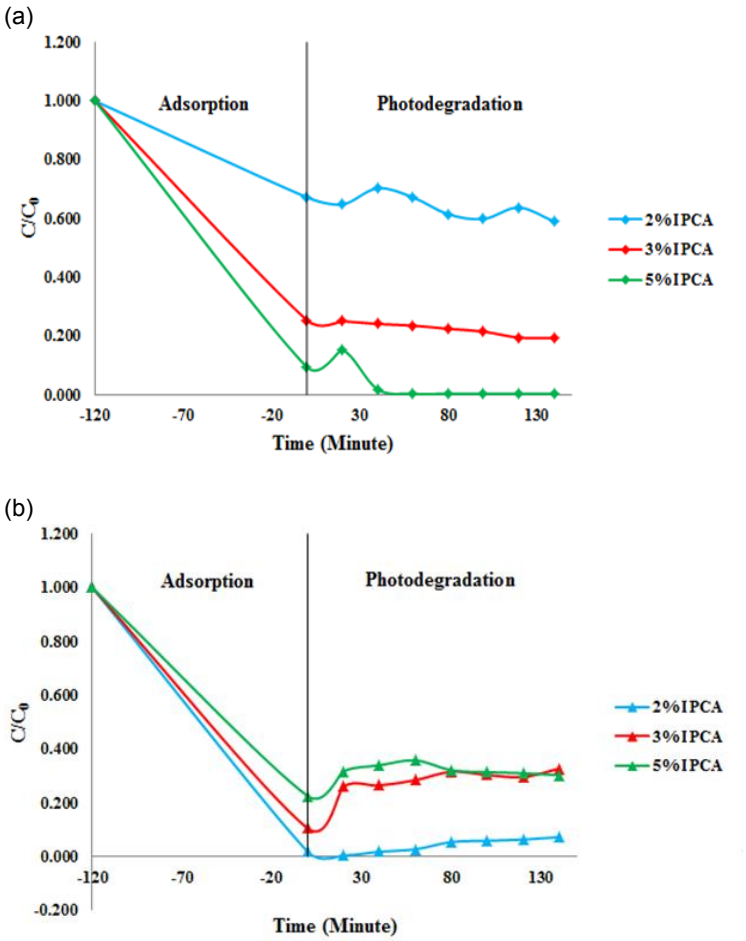

Figure 3: Effect of GO ratios on $LaFeO_3$ on photodegradation of (a) methylene blue and (b) methyl orange dye

Meanwhile, under visible light irradiation, as shown in Figure 3a and 3b, photocatalytic activity showed effective removal of MB compared to MO removal. It can be seen that, increasing the ratio of GO from 2 % until 5 % gives out removal percentage values of 12 %, 24 % and 100 % (Ismail et al., 2009). This caused by increasing the availability of active sites on surface and number of photons absorbed (Wahab and Hussain, 2016). Despite higher adsorption rate in both dyes, low photocatalytic activity could be observed. The photocatalytic activity for MO conducted by all ratios also reached equilibrium after 80 min and no further removal were detected. This is mainly due to the shielding effect of dye molecules to the photocatalyst particles (Pal et al., 2016). The shielding effects limit the adsorption of photons on the surface of the photocatalyst, thus reduced or inhibit the photocatalytic activity.

4. Conclusions

In this study, $LaFeO_3$-GO composites was prepared using of lanthanum nitrate hexahydrate ($La(NO_3)_3.6H_2O$) and iron (III) nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$) as precursor; glucose as a complexing agent and graphene oxide (GO). MB and MO dyes were selected as targeted pollutants for integrated adsorption and photocatalytic effect on removal of synthetic dyes. For adsorption process, the relationship between methylene blue dye's adsorption rate and GO content followed the sequence: 5 % > 3 % > 2 % while for methyl orange dye, it showed that adsorption rate of MO dye increased with decreased in GO ratios on $LaFeO_3$. Somehow, superior adsorption could be observed in $LaFeO_3$-GO composites for MO dyes. For photocatalytic activities, methylene blue showed higher degradation compared to methyl orange. Throughout this study, optimum ratio of 5 % of GO deposited on $LaFeO_3$ successfully removed 100 % methylene blue for 60 min. Integrated between photocatalysis and adsorption can be seen as potential combination for removal of synthetic dyes in future.

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