Presented at the DLSU Research Congress 2019
De La Salle University, Manila, Philippines
June 19 to 21, 2019

Green Synthesis and Characterization of Magnetic Pectin-Iron Oxide Nanocomposite and its Application in the Adsorptive Removal of Dyes

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Abstract: Green synthesized magnetic pectin-iron oxide nanocomposites (MPION) was used as an adsorption agent for the removal of common toxic dyes found in waste water from textile industries, namely Methyl violet, and Methylene blue. Pectin, a polysaccharide found in fruits, was extracted from *Citrus maxima* (Pomelo) peels and was utilized to coat the green synthesized iron oxide nanoparticles (ION). The characterization of the MPION was carried out by Fourier transform infrared spectroscopy. The nanocomposite was placed in the prepared dye solutions. The absorbance of the dyes was taken using UV-Vis Spectrophotometry. The initial absorbance along with the absorbance after the addition and removal of MPION was measured and recorded for the computation of concentrations of the dye solutions. It was found that the adsorptive capacity of (MPION) was significantly greater than the ION for Methyl violet and Methylene blue.

Key Words: magnetic iron oxide; nanocomposite; pectin; dye remediation;

1. INTRODUCTION

Water is essential for survival. Looking into the water reservoir of the earth, only 2.5% of the total water resources is freshwater and only 1% to 2.5% of the drinkable water is accessible to humans (Mishra & Dubey, 2015). Amidst subdued resources of potable water, many societies overlook potential sources of water, a limited commodity which is a necessity for the life of all species.

According to Shannon, et al. (2008), 15% of the world's population lack access to potable water. With the expeditious expansion of industrialization, ensuring access to the limited potable water has been a severe challenge in the world for the widespread effect of water pollution is dramatically affecting all sectors of society.

The contamination of water with several pollutants such as heavy metals, inorganic chemicals, and dyes can cause fatality within species. (Wu, Feng, Wang, & Wang as cited in Sehlleier, Hardt, Schulz, & Wiggers, 2016). According to Drumond-Chequer, et al. as cited in Oliva, et al. (2018), at least 10,000 different dyes and pigments are used by textile industries which contaminate 200,000 tons of water. A few examples of these dyes are Methylene Blue (C16H18N3SCl), a cationic dye that can cause increased heart rate, vomiting, Heinz body formation, cyanosis, jaundice, and tissue necrosis (Popa & Visa, 2017) and Methyl violet (C24H28N3Cl), a basic dye that can inhibit photosynthesis of aquatic plants (Hameed as cited in Xu, Xiao, Yuan, & Zhao, 2011). This data can deduce problems of water contaminated with textile dyes.

One of the methods to alleviate the problem is dye remediation. According to Peres, Slaviero, Cunha, Hosseini-Bandegharaei, and Dotto (2018), dye adsorption is the adsorption to an absorbent of dye molecules from an aqueous solution. Nanoparticles showed promise in adsorption capacity characterized by its small size, magnetic property, and reusability (Hasany, Ahmed, Rajan, & Rehman as cited in Nanta, Kasemwong, & Skolpap, 2018). Looking into the magnetic property, the retrieval of the Iron oxide nanoparticles can be achieved since only a magnetic field is needed to retrieve the sample (Venkateswarlu, et al. as cited in Bishnoi, Kumar, & Selvaraj, 2018).

2. METHODOLOGY

2.1 Preparation of Citrus maxima peel powder

Citrus maxima samples were purchased from a local supermarket. Mature *Citrus maxima* fruits were skinned to separate the exocarp and albedo. Then, the mesocarp of the fruit was obtained and ground using mortar and pestle. The initially pulverized mesocarp was then exposed to direct sunlight to terminate microbial activity and enhance the evaporation process of the sample. A double crimp screen mesh was used to prevent decomposers from infecting the sample. With this, a crisp-like structure of the mesocarp of the *Citrus maxima* was obtained.

Thereafter, another round of grinding using mortar and pestle was done to further augment the powder composition of the sample. The samples were then stored in zip-lock containers to prevent the sample from absorbing moisture from the air. Also, the researchers stored the sample in a refrigerator not exceeding the temperature of 4°C for further testing.

2.2 Pectin Extraction

Pectin was extracted from *Citrus maxima* peels, 4 grams of finely ground peels was used. The powder was mixed in 320 mL of distilled water in a 1000 mL beaker. The pH of the solution was modified to a pH of 2 using 1M H_2SO_4. The mixtures were placed in the microwave (Samsung, Model ME711K) with power 450W for 4 minutes. After heating, both mixtures were immediately filtered. 98% ethanol solution was then added to the supernatant at a 1:2 solution to ethanol ratio (Fig. 1). The mixtures were refrigerated for more than 24 hours for crystallization to occur. After refrigeration, the mixtures were filtered using a Buchner funnel and the residue collected were washed with 98% ethanol. The residue was dried using an oven set at 50º C overnight.

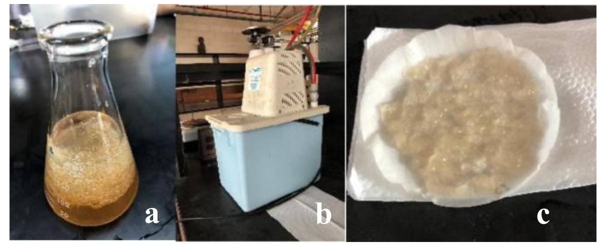

Fig 1. From left, (a) Supernatant of the mixture with 98% ethanol, (b) Buchner funnel, (c) Extracted Pectin.

2.3 Synthesis of Magnetic Pectin-Iron Oxide Nanocomposite

The synthesis of magnetic pectin-iron oxide nanocomposite was performed using the methods of Gong, et al. (2012) with a few modifications. Iron oxide was prepared by mixing 0.1M of Iron (II) sulfate ($FeSO_4 \cdot 7H_2O$) and 0.2M of Iron (III) chloride, hexahydrate ($FeCl_3 \cdot 6H_2O$) with 1% (w/v) of pectin in 50 ml of purged distilled water heated at 90ºC (Fig. 2).

Fig 2. From left, (a) $FeSO_4$, (b) $FeCl_3$, (c) set-up for purging.

The solution was then purged for 10 minutes. 5 mL of 25% ammonia was added to the solution with continuous stirring. After the reaction was completed, the black precipitate was gathered using a permanent magnet. The collected precipitate was washed using distilled water and dried at 50ºC - 70ºC for 24 hours. The magnetic pectin-iron oxide nanocomposite (MPION) was obtained by grinding the black precipitate to a powder-like consistency.

2.4 Characterization

The obtained magnetic pectin-iron oxide nanocomposite was subjected to Fourier-transform infrared spectroscopy (FTIR) to scan its chemical properties and assess the chemical composition of the synthesized material.

2.5 Adsorption Tests

For the adsorption test, two dyes were used: Methylene blue, and Methyl violet. A stock solution of 0.001M of each dye was used. Using Beer's Law, the concentration is directly proportional to absorbance. 5 serial dilutions of the stock solution were used for the measurement of absorbance and determination of the standard curve using UV-Vis spectrophotometer in the 663nm wavelength for Methylene Blue and 579nm wavelength for Methyl Violet.

The 8.0×10^{-6} M concentration of Methylene blue and 4.0×10^{-5} M concentration for Methyl violet was used. The initial absorbance was recorded using UV-Vis spectrophotometer. About 2 grams of magnetic pectin-iron oxide nanocomposite was added into the dye solution and incubated for 24 hours. After that, the MPION was separated using a permanent magnet and the absorbance of the resulting solution was recorded using UV-Vis spectrophotometer. The standard curve and the coefficient of determination were used to determine the concentration of the resulting dye solution.

The percent removal of MPION was computed following the formula:

$$\%removal = \frac{C_0 - C_f}{C_0} \times 100$$

3. RESULTS AND DISCUSSION

3.1 Synthesis of MPION

Particles that were synthesized using iron (II) sulfate ($FeSO_4 \cdot 7H_2O$) and iron (III) chloride, hexahydrate ($FeCl_3 \cdot 6H_2O$) immediately formed after the addition of ammonia solution. It was observed that the resulting mixture for the Iron oxide nanoparticles, MPION with extracted pectin, and MPION with commercial pectin were a deep black color (Fig. 3) due to the reduction reaction. This is in line with the description of Prasad (2016) on Iron oxide nanoparticles.

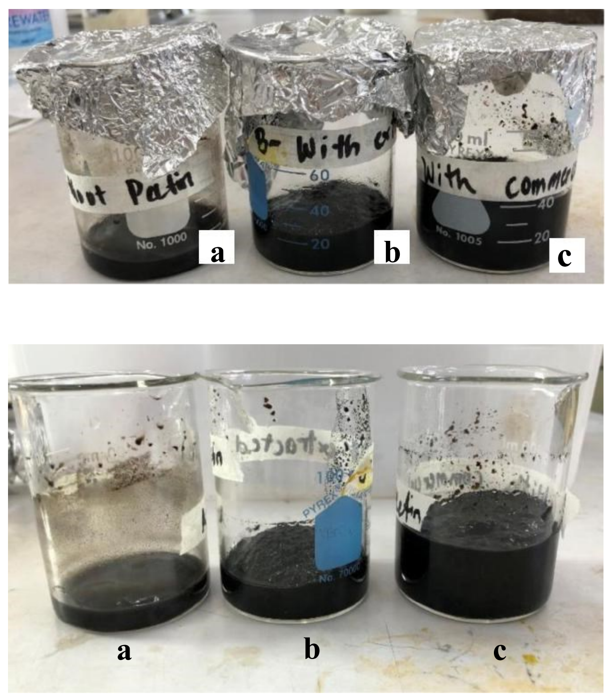

Fig 3. From left, (a) magnetic Iron oxide nanoparticles, (b) magnetic Iron oxide nanocomposite with extracted pectin, (c) magnetic Iron oxide nanocomposite with commercial pectin.

It is observed from the Iron oxide nanoparticles (Fig 1.a) that it has fine powder-like texture compared to the MPION with extracted pectin (Fig 1.b) and MPION with commercial pectin (Fig 1.c), which contains particles that are clumped together. When subjected to a magnetic field, all the samples were attracted to the magnet. It was also observed that Iron oxide nanoparticles have a stronger attraction towards a magnetic field compared to MPION with extracted pectin and MPION with commercial pectin. According to Namanga, Foba, Ndinteh, Yufanyi, and Krause (2013), this may be due to the increased interparticle distance between the magnetic nanoparticles, which influences the strength of the magnetic interaction.

3.2 FTIR Analysis of MPION

FTIR spectra of the green synthesized magnetic pectin-iron oxide nanocomposite is shown as Fig. 4, Fig. 5, and Fig. 6. The functional groups responsible for the synthesis of the nanocomposite were identified using the FTIR spectra data. The spectra of Iron oxide nanoparticles, MPION with commercial pectin, and the MPION with extracted pectin were compared. The peaks at 3454.12cm^{-1}, 3429.22 cm^{-1}, and 3424.25 cm^{-1} all correspond to the presence of strong alcohol groups mainly O – H stretching. At the wavenumbers 2921.38 cm^{-1}, and 2923.92 cm^{-1} for the iron oxide nanoparticles and MPION with commercial pectin, respectively, shows an alkane functional group, more specifically a C – H sp^3 while only MPION with extracted pectin showed a peak in 3186.45 cm^{-1} which corresponds to the alkene group C – H sp$_2$ (=C – H). This observation implies that the extracted pectin was integrated into the MPION with extracted pectin since the presence of alkene is usually found in pectin (Gnanasambandam & Proctor, 2000)

The peaks that differ from the three samples define each sample's properties and composition. The iron oxide nanoparticles showed a moderate peak in the 1635 cm$_{-1}$ which is due to an asymmetric COO – stretching. This peak has been observed with Iron oxide nanoparticles from the study of Sathya, Saravanathamizhan, & Baskar (2017). For the MPION with commercial pectin, a moderate peak was observed at a wavenumber of 1402.85 cm^{-1} along with a peak at 1635.46 cm^{-1}. This indicates that both symmetric and asymmetric COO – stretches were observed. This might be due to the addition of commercial pectin to the Iron oxide nanoparticles. The peaks observed in MPION with extracted pectin was in the wavenumber 1740.47 cm^{-1} which corresponds to the esterified C=O commonly found in pectin. These observations demonstrate that magnetic pectin-iron oxide nanocomposite was synthesized with extracted pectin from *Citrus maxima* peels.

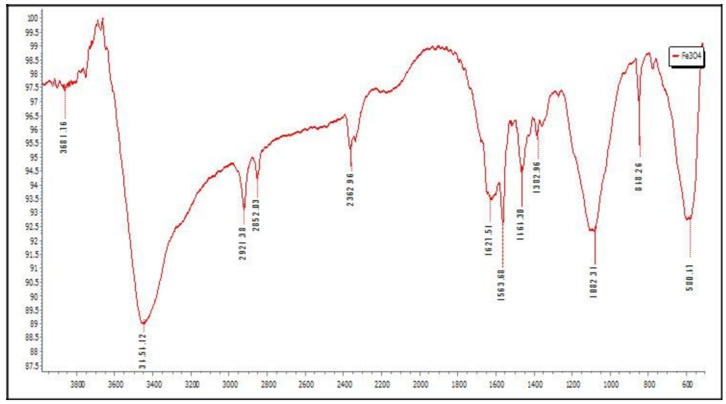

Fig. 4. FTIR spectrum of Iron Oxide Nanoparticles.

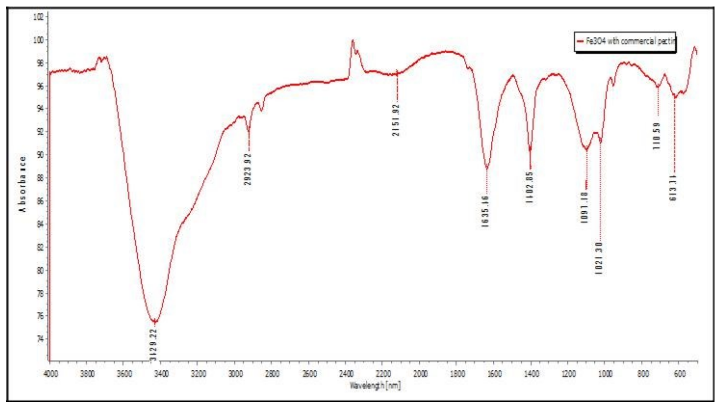

Fig. 5. FTIR spectrum of Magnetic Pectin-Iron Oxide Nanocomposite synthesized with commercial pectin.

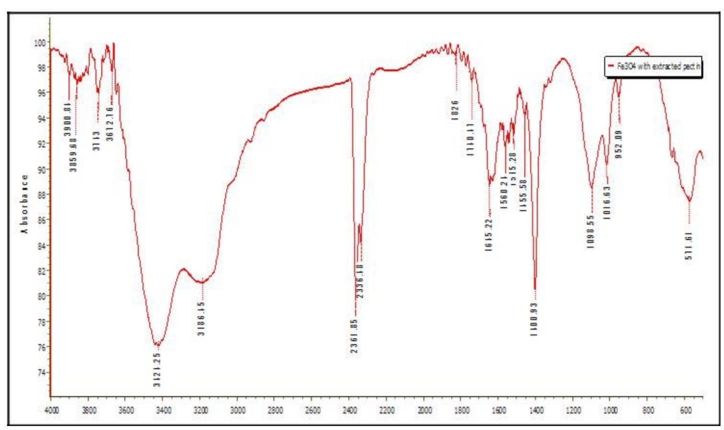

Fig. 6. FTIR spectrum of Magnetic Pectin-Iron Oxide Nanocomposite synthesized with extracted pectin.

3.3 Dye Adsorption

UV-Vis Spectrophotometer was used to determine the initial and final absorbance of the dye dilution. Following Beer's Law, the concentrations were computed. Fig. 7 and Fig. 8 shows the standardized curve for Methyl violet and Methylene blue, respectively. The graph also shows the coefficient of determination (R^2) of the standardized curve.

For methyl violet, the calculated percent removal was 12.14% using the MPION with extracted pectin. This is significantly higher than the calculated percent removal of MPION with commercial pectin. This value would infer that the extracted pectin was a better adsorbent than the nanocomposite synthesized with commercial pectin.

The results for methylene blue revealed a value of 39.9% removal using the MPION with extracted pectin, while MPION with commercial pectin was only 22.0%, which is significantly lower. The adsorption in this dye is also more efficient with MPION with extracted pectin as compared to the MPION with commercial pectin.

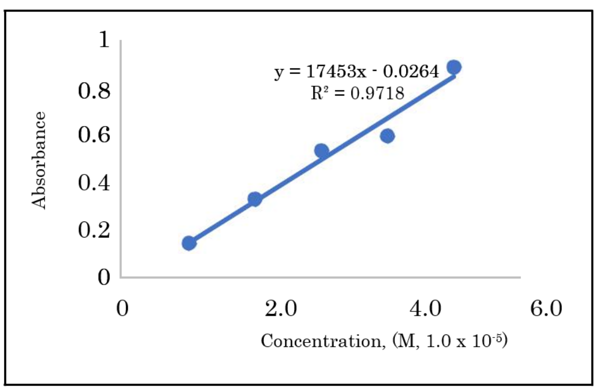

Fig. 7. Concentration vs Absorbance graph, with the regression line for Methyl Violet.

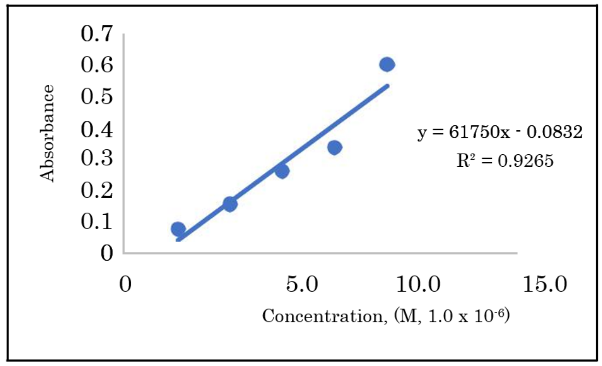

Fig. 8. Concentration vs Absorbance graph, with the regression line for Methylene Blue.

4. CONCLUSIONS

Pectin, a heteropolysaccharide, was successfully extracted using microwave-assisted extraction from *Citrus maxima* peels. Pectin, both commercial and extracted were able to coat iron oxide nanoparticles to form a nanocomposite. The properties of Iron oxide nanoparticles, MPION with commercial pectin and MPION with extracted pectin were all observed using FTIR spectra analysis. It was shown that the pectin was able to coat the nanoparticles due to certain percentage transmittance peaks from the spectra analysis commonly found in pectin alone. In this study, the adsorptive capacity of the MPION was tested and the results gathered data that MPION was able to adsorb dyes which are commonly found in waste water.

5. ACKNOWLEDGMENTS

The authors would like to thank the Senior High School and Chemistry Departments of the De La Salle University for the support.

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