Synthesis of graphene oxide from industrial waste

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Abstract. This paper investigates a synthesis of graphene oxide (GO) from industrial waste via leaching and modified Hummers method. In leaching process, most of the impurities were effectively removed by dissolving into 6 M HCl at 70 °C for 210 mins to produce 92.28 % purity graphite residue. Subsequently, GO was synthesis via modified Hummers method with a combination of concentrated H_2SO_4 and $KMnO_4$. The result from XRD and FTIR analyses confirmed that GO was successfully synthesized. Additionally, a monolayer and multilayer GO with wrinkles surface was observed by TEM which evident the existence of GO surface morphology.

Keywords: Industrial waste, leaching, modified Hummers method, graphene oxide

1. Introduction

Malaysia is a rising developing country that relies on the industrial productivities as one of the contributors towards country's economy. In the transition process of industrialization, variety of wastes will be generated such as electronic scrap, metal finishing industrial waste, spent petroleum catalyst, and battery waste [1]. However, by using hydrometallurgical method which also known as leaching, some valued materials (e.g. graphite, Cu, Fe, and Zn) from the industrial waste can be recovered [2]. Graphite is not well being known as a valuable element to the layman public but it is foreseen to be the wonder material in 21st century just as plastic was considered crucial in the 20th century. This prevision was manifested by the potential of graphite- based materials for application in different fields due to their unique physical and chemical properties such as chemical inertness, thermal stability, high electrical conductivity, and lubricity that allows it to be applicable in many industrial applications including electronics, lubricants and metallurgy [3–6]. Moreover, graphene oxide, GO is one of the main research branches from graphite due to its low cost, easy access and widespread ability to convert to graphene [7]. GO consists of a single monomolecular layer of graphite with various oxygen contained functionalities, such as OH, C = O and C – O – C groups [8]. The presence of oxygen functionalities in GO makes GO easily disperse in water and organic solvents [9]. This advance property makes GO has benefit as an additive on ceramic and polymer manufacturing process in enhancing their electrical and

mechanical properties such as tensile strength, elasticity and conductivity [10]. Besides that, GO and its composites provide alternate applications such as energy storage/conversion and environmental protection, including hydrogen storage materials, photocatalyst for water splitting, removal of air pollutants and water purification, as well as electrode materials for various lithium batteries and super capacitors [11]. Moreover, GO can be applied in oil and gas industry as an additive for drilling fluid, cementing, enhanced oil recovery, desalination, oil spill clean-up, and emulsion stabilization [4]. Additionally, GO can improve fluid loss control, rheology, lubrication, and shale stability [12].

As a highly developing country, Malaysia produces approximately 168 million tons of municipal solid waste (MSW) annually including agriculture and industrial [13]. This value shows that the rapid industrialization has subsequently contributed to the waste generation which enhance a demand in waste utilization/recycling. Therefore, a recent challenge is to find efficient waste utilization processes that can be used to convert industrial waste to value added material (i.e. GO) by removing hazardous metal impurities in it. However, there are still some limitations on the existing method of GO synthesis. One of them is the application of Hummers and Tour methods exhibited longer experimental time (approximately 10 hours per batch) with the formation of toxic gas (e.g. NO). This condition occurred due to the utilization of $NaNO_3$ as an oxidant agent [14–17]. Thus, this study intends to improve the existing method of GO synthesis by ensuring optimum experimental time at maximum production of GO under the environmental friendly condition. Essentially, the objectives of this study are: to extract graphite from industrial waste through leaching method and to synthesis the GO from graphite residue via modified Hummers method.

2. Methodology

2.1. Material
Industrial waste was used as the raw material for GO synthesis. Mechanical grinder (Vigor mix 700 Swing Type Dry Grinder) and GILSON 106 µm stainless steel test sieve were used to obtain 106 µm powder slag. Before the purification, the industrial waste sample was analyzed using energy dispersive X-ray, EDX to identify the elemental content and the initial purity of graphite.

2.2. Leaching experiment
Separately, 10 g of industrial waste was leached in 6 M HCl with liquid to solid of 1:10 at three different temperatures (30 °C, 50 °C and 70 °C) for 210 mins. A modified Heidolph Hei-VAP Platinum 2 Rotary Evaporator was used to conduct the leaching experiment. After leaching test, the solid residues were filtered in glass funnel by using Whatman filter paper (125 mmΦ) and neutralized with MilliQ ultrapure water until pH 7. Resulted residue was then dried in oven at 60 °C for 24 hrs and then the residue was subjected for analysis of graphite purity. The impurities removal (%) is calculated based in equation (1) and the sample was collected for analyses at every 30 mins throughout the leaching process.

$$\text{Removal (\%)} = [L] / [R] \times 100 \% \tag{1}$$

where *[L]* is the elemental concentration of metal in liquid leachate in ppm and *[R]* is the elemental concentration of metal in raw material (industrial waste) also in ppm.

2.2.1. Kinetic model determination.
Shrinking core model is one of the most common models that use to describe the leaching mechanism through non-catalytic reaction relations between solid particle and solvent [18–20]. The most common kinetic reactions are first and second order reaction as expressed in equations (2) and (3):

$$kt = ln\,(1 - x); \text{ first-order reaction} \tag{2}$$

$$kt = x / (1 - x); \text{ second-order reaction} \tag{3}$$

where x is the reaction fraction (removal percentage), k is the kinetic constant and t is the reaction time.

According to the Shrinking core principle, the leaching mechanism may undergoes 3 main different steps which consist of diffusion of leaching agent through surrounding film of the particle, diffusion of leaching agent through product to the unreacted core surface and reaction with the particle on its surface as delineated in equations (4) – (6) respectively [18–21]. In this study, leaching mechanism is identified based on the highest correlation coefficient (R^2) obtained based equations (4) – (6).

$$kt = x \tag{4}$$

$$1 + 2 (1 + x) - 3 (1 - x)^{2/3} = kt \tag{5}$$

$$1 - (1 - x)^{1/3} = kt \tag{6}$$

2.3. GO synthesis

A modified Hummers method [4,22] was adapted to synthesis the GO from graphite residue obtained via leaching of industrial waste as explained in Section 1.2. In the synthesis process, concentrated H_2SO_4 (30 mL) and graphite residue (1g) were mixed homogenously in ice bath for 30 mins. 5g of $KMnO_4$ was added to the solution and mixed at temperature less than 10 °C for another 15 mins. At this step, ratio of $KMnO_4$ was modified from 1:3 [23] to 1:5 to promote oxidation process subsequently terminating the use of $NaNO_3$. 8 mL of ultrapure water was then added dropwise for 15 mins and the temperature of reaction was kept lower than 98 °C for about 1 hr. Finally, the oxidation reaction was terminated with the addition of 60 mL ultrapure water followed by 1 mL H_2O_2. The termination process took approximately 15 mins by monitoring the disappearance of bubble in the mixed solution. After that, the solid powder was filtered and subjected to repeated washing with 5 % of HCl solution and distilled water to remove impurities. The resulted solid powder was dried at 60 °C for 24 hours and subjected for the characterization analysis. Table 1 tabulates some modification and improvement that has been made based on experimentation time for each GO synthesis steps.

Table 1. Comparison between the previous and present study of Hummers method.

Process	Present study (experimentation time, mins)	Previous study (experimentation time, mins) [15,16,24]
Mixing process	30	60
H_2SO_4 and graphite residue		
Oxidation	15	60
Addition of $KMnO_4$		
Hydrolysis	60	180
Addition of H_2O		
Termination	15	30
Addition of H2O and H_2O_2		

Total time, min	150	330

2.4 Characterization

The final solid powder samples were characterized using various analytical method including Fourier transform infrared spectroscopy (PerkinElmer Spectrum GX-FTIR), X-ray diffraction (XRD) using D8 Focus XRD diffractometer and Transmission electron microscopy (Hitachi HD2000 TEM, accelerating voltage 20.00kV equipped with an energy dispersive X-ray (EDX) detector).

3. Result and discussion

3.1. Leaching of industrial waste

Table 2 shows elemental analysis for the raw material (industrial waste) and graphite residue obtained from the leaching process. EDX detected five major impurities consisted of heavy metals (Fe, Cr, Mn and Cu) and silica. It is expected that the highest weighted percentage of impurities in industrial waste was exhibited by the heavy metals (impurities) as tabulated in Table 2. It can be noticed after the leaching process, most of the impurities can be effectively removed by using HCl acid subjected to three difference temperatures (30 °C, 50 °C and 70 °C). According to Fig. 1, total impurities removals (%) were increased throughout the leaching process. However, it can be observed that the highest percentage of impurities removal occurred at 70 °C with 6 M HCl, liquid to solid ratio of 1:10 and leaching time of 210 mins. This result indicated that the dissolution rate was increased with the increment of temperature. Moreover, high temperature could enhance the leaching rate since the complexity of impurities compound would decompose at higher temperature [25]. Reaction Equations (7) – (9) describe the simple leaching mechanisms of metal impurities in industrial waste (i.e., Fe).
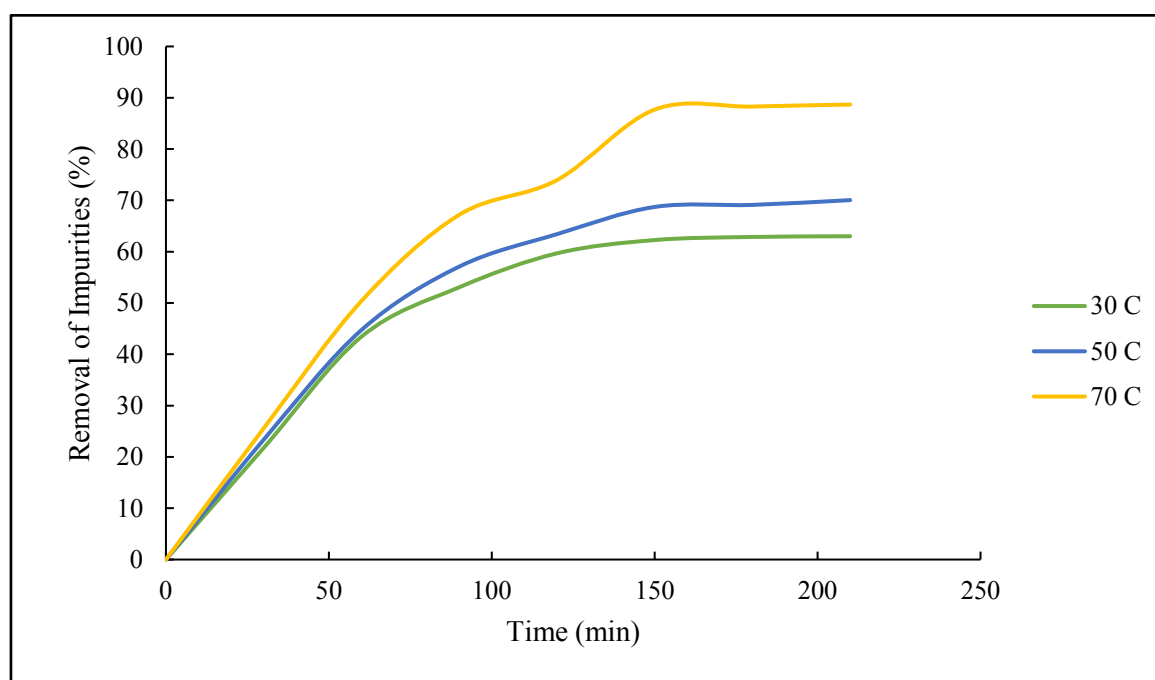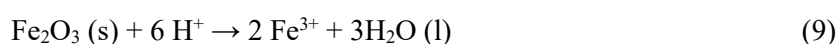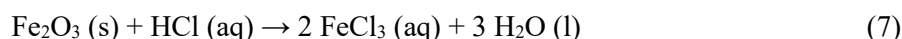
$$Fe_2O_3 \text{ (s)} + HCl \text{ (aq)} \rightarrow 2 \text{ } FeCl_3 \text{ (aq)} + 3 \text{ } H_2O \text{ (l)} \tag{7}$$

$$Fe_2O_3 \text{ (s)} + 6 \text{ } H^+ + 6 \text{ } Cl^- \rightarrow 2 \text{ } Fe^{3+} + 6 \text{ } Cl^- + 3H_2O \text{ (l)} \tag{8}$$

$$Fe_2O_3 \text{ (s)} + 6 \text{ } H^+ \rightarrow 2 \text{ } Fe^{3+} + 3H_2O \text{ (l)} \tag{9}$$

Figure 1. Effect of leaching time on impurities removal at different temperatures.

Table 2. Element analysis of industrial waste and leached residue.

Element	Industrial waste		Leached residue	
	Weight, %	Atomic, %	Weight, %	Atomic, %
C	18.78	30.80	90.81	92.28
O	26.09	37.98	2.95	4.29
Fe	21.20	8.45	2.40	0.96
Cu	2.11	0.66	0.24	0.07
Si	0.86	0.86	0.86	0.86
Cr	11.75	6.38	1.33	0.72
Mn	12.48	7.23	1.41	0.82
	100		100	

3.1.1. Leaching kinetic mechanism. Identification of kinetic mechanism for leaching process is important to identify the leaching behaviour and mechanism which important for GO synthesis process. Figures 2 – 4 depict the profile of leaching kinetic model based on the optimal condition (highest impurities removal) obtained in the leaching process (70 °C with 6 M HCl, liquid to solid ratio of 1:10 and leaching time of 210 mins) using three different types of kinetic model as showed in equations (4) – (6). It can be observed that the highest correlation coefficient (R^2) value (indicate close to linearity $\approx$ 1) was exhibited in figure 3 at R^2 averaged value at 0.933 if compared to figures 2 and 4. This result indicated that HCl leaching process conducted in this study was followed the diffusion of leaching agent through product to the unreacted core surface mechanism [18,19,21].
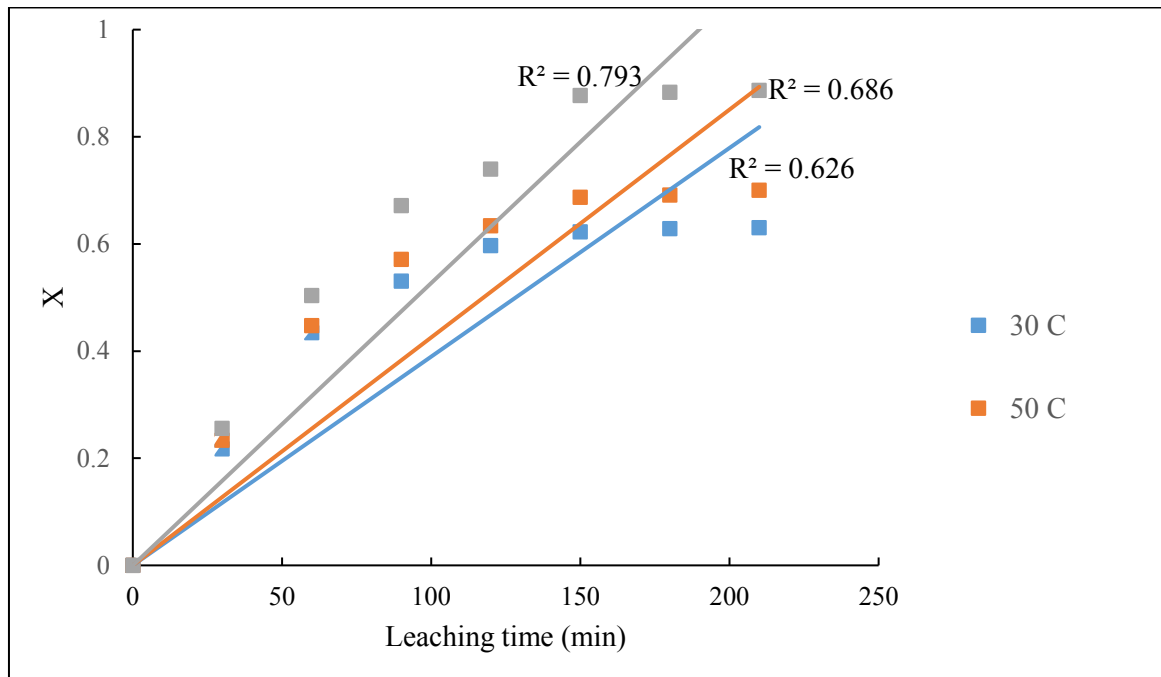
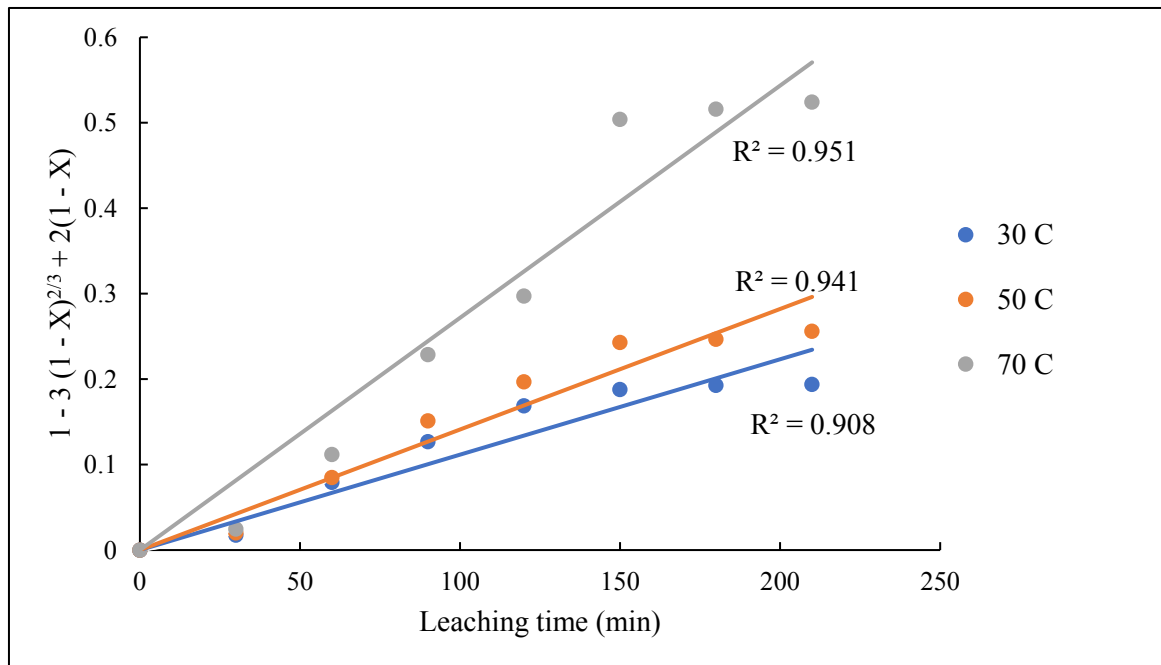**Figure 2.** Variation of X with the time at different temperatures.

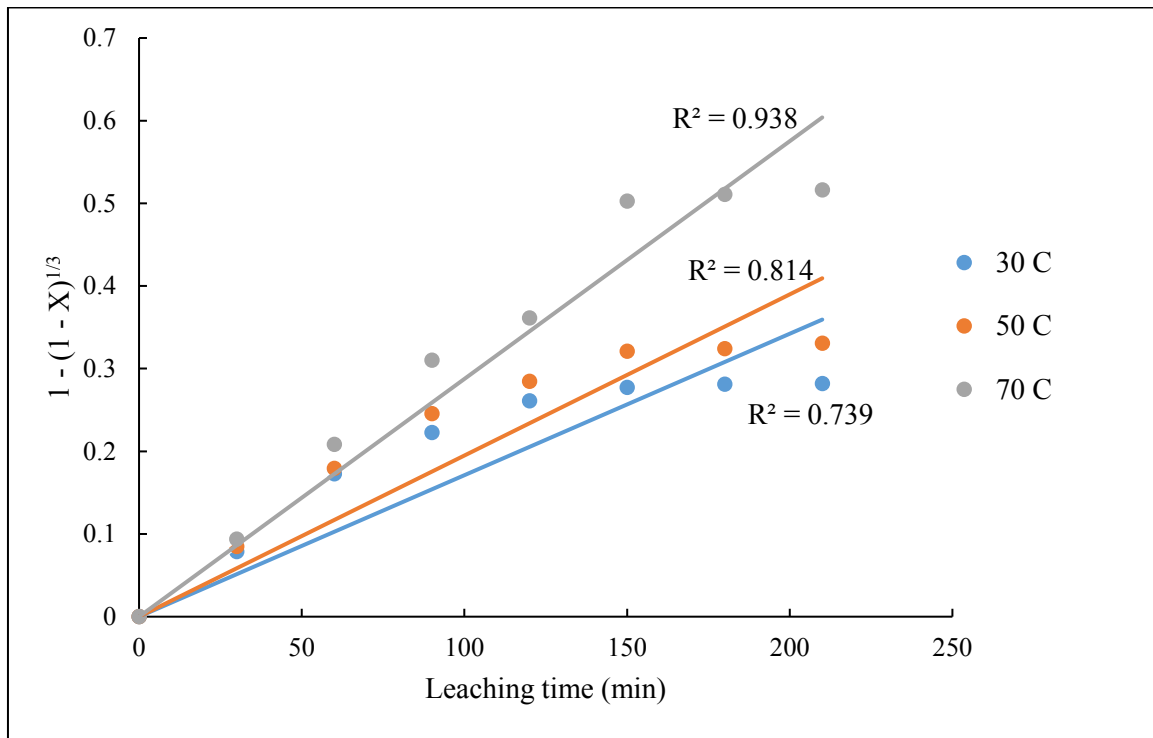**Figure 3.** Variation of $1-3(1-X)^{2/3}+2(1-X)$ with the time at different temperatures.

Figure 4. Variation of $1 - (1 - X)^{1/3}$ with the time at different temperatures.

3.2. GO synthesis and characterization

A thin black layer of GO was successfully obtained as illustrated in figure 5. This underpinned with the similar thin layer obtained in the previous study conducted by LingSun and Bunshi (2013) [26].

Figure 5. Layer of GO.

Figure 6 shows the XRD analysis of crystalline nature graphite and GO. The XRD pattern of the graphite in industrial waste shows a diffraction peak at $2\Theta = 26.6\,°$ corresponding to an interlayer spacing of 0.34 nm. The transformation of graphite into GO has corresponding change in the XRD peak from 2Θ value of $26.6\,°$ to $10.35\,°$ with d-spacing of 0.73 nm. These findings supported by the study conducted in [14,22,27]. From this analysis, it also can be observed that there are a consistency with the

interlayer spacing of GO, due to the presence of oxygen functional groups and water molecules cornered between the sheets.
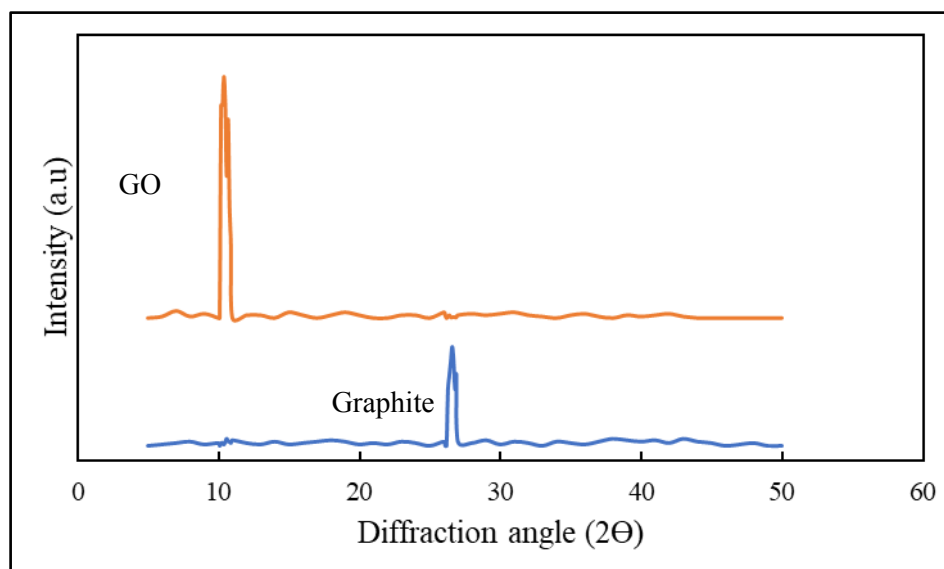

Figure 6. XRD pattern of graphite and GO.

Figure 7 shows the FTIR analysis and spectra of GO. The objective of the analysis is to identify different types of functional groups formed in GO. As depicted in the figure, a C – H stretching of –CH_3 and –CH_2 occurred in adsorption peak ranging from of $800 – 1240$ cm^{-1} while the appearance of C = C groups were at the peak value of 2139 cm^{-1} and the C – C stretching appeared in peaks range of at $1615 – 1640$ cm^{-1}. While, a peak range from $3000 – 3400$ cm^{-1} indicated the O – H stretching. Similar FTIR spectra can be observed in the study conducted by [9,28].
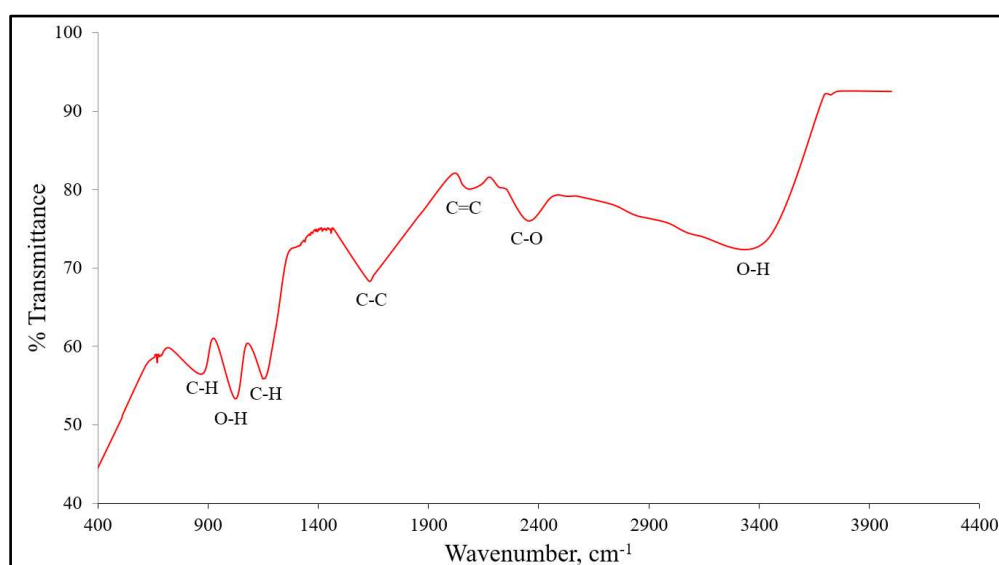

Figure 7. FTIR spectra of GO.

The surface morphology and crystalline nature of the synthesized GO was analyzed using TEM as exhibited in figure 8. The TEM images show a monolayer (figure 8(a)) and multilayer GO (Figure 8(b))

by observing the fold back and cross sectional lines using TEM at several locations. It also shows a high electron transparent corrugated and wrinkled structure of GO layer. The surface morphology of GO which consist of thin stacked flakes is well defined multilayer structure at the edge that can be clearly observed. This result indicated that, with the increases in the oxidation level, GO will become highly transparent due to the existing of high amounts of oxygenated functional groups, which produces monolayers or multilayer of GO after ultrasonication [9,29].
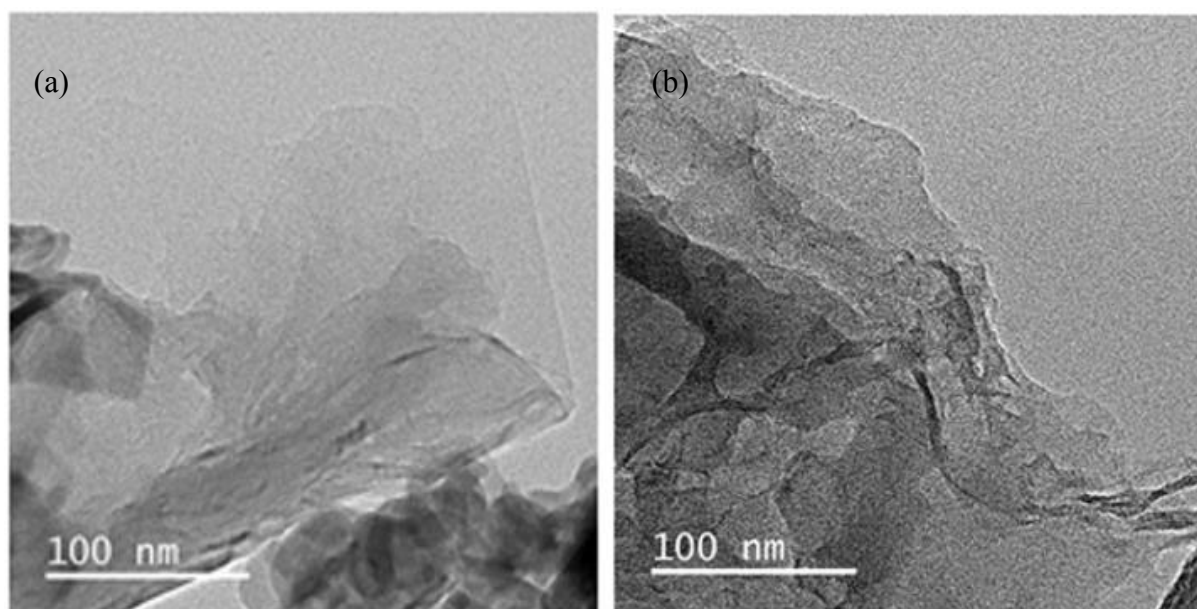

Figure 8(a). TEM images of synthesized monolayer GO. (**b).** TEM images of synthesized multilayer GO

4. Conclusion

This study reveals that the impurities contained in industrial waste can be effectively removed by HCl acid leaching treatment of 6 M HCl at temperature of 70 °C with solid to liquid ratio of 1:10 for 210 mins. Monolayer and multilayer GO were successfully synthesized by using modified Hummers method. The XRD spectra showed that the GO has a low degree of crystallinity with $2\Theta = 10.35$ ° and d-spacing of 0.73 nm. The main functional groups peak signal (O – H, C – C, C – O) also can be found in FTIR analysis which strongly confirmed the existence of GO.

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