Synthesis of iron modified sugarcane bagasse activated carbon for oxidation degradation of malachite green

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Abstract. Iron (II, III) oxide (Fe₃O₄), activated carbon (AC) and Fe₃O₄/AC composites at various weight ratios (1:1, 3:1 and 1:3) were synthesised successfully using chemical impregnation method. The synthesised composite samples were then analysed by using scanning electron microscope coupled with energy dispersive X-ray (SEM-EDX), X-ray diffraction (XRD) and fourier transform infrared spectroscopy (FTIR). Heterogeneous photo Fenton and Fenton-like processes were applied in degrading malachite green. Fe₃O₄/AC composite samples showed higher catalytic activity as compared to pure Fe₃O₄ and AC. The composite of Fe₃O₄/AC at weight ratio of 1:1 (FeAC11) was determined to be the optimal mixing weight ratio as it possessed the highest heterogeneous photo Fenton and Fenton-like degradation efficiency of malachite green. The highest degradation efficiency of malachite green was achieved at initial dye concentration of 30 ppm, FeAC11 dosage of 0.8 g/L, solution pH of 5, 4 mM of H₂O₂ with the degradation efficiency of 89.22 % after 3 min. The composite sample FeAC11 depicted high stability as only little amount of leached iron (about 4 mg/L) was detected by inductively coupled plasma optical emission spectrometry (ICP-OES). Pseudo second-order kinetic was best fitted to the reaction kinetic of heterogeneous photo Fenton and Fenton-like on the degradation of malachite green at different solution pH.

1. Introduction

The discharge of effluents containing dyes have caused both health and environmental effect. Detrimental side effects on health of aquatic and human could be happened with even just 1 ppm of dye concentration due to the carcinogenic and mutagenic properties of dye [1]. It was reported that a portion of dyes (10-20 %) during dyeing stage would discharge as industrial effluent due to the incomplete fixation of dye on fibres. The dyes lost to the water source is difficult to be degraded by using conventional methods [2]. Hence, it is essential to develop an environmental friendly and energy efficient technique to treat the effluents consisting of organic dyes before discharging to environment [1].

Fenton and Fenton-like processes which involve the use of iron ions (Fe²⁺/ Fe³⁺), are considered as one of the most cost-effective advance oxidation processes (AOPs) to degrade the organic dyes [3]. To overcome few issues such as undesired sludge and narrow range of pH accessibility [4], heterogeneous instead of homogeneous Fenton and Fenton-like processes are selected for this study. The
heterogeneous Fenton and Fenton-like degradation processes can be enhanced with the presence of light source. The involvement of both photocatalysis and heterogeneous Fenton and Fenton-like processes are termed as heterogeneous photo Fenton and Fenton-like processes. Sugarcane bagasse was opted as the AC source due to it is the largest agriculture crop over the globe. After harvesting the sugarcanes, the tops and leaves are left in the field and the stalks will be transported to the mill, followed by crushing process to extract the sugar juice for the sugar production process. As a result, there will be two residues generated, which are bagasse (the fibrous fraction following juice extraction) and straw (the harvest residue). In general, there are about 280 million metric tons of straw and bagasse yielded every year [5]. As one of the environmental friendly means to handle such huge amount of bagasse, it can be transformed into higher value products such as AC source. Sugarcane bagasse with rich carbon content are suitable to be used as the supporter for metallic catalyst particles in a stable and active manner.

In this research, iron modified sugarcane bagasse AC were synthesised through the chemical impregnation method. Composite samples at various weight mixing ratio between Fe3O4 and AC were synthesised to determine the optimum proportion in degrading the malachite green via heterogeneous photo Fenton and Fenton-like processes.

2. Experimental

2.1. Materials
Malachite green (99 %) was acquired from Fisher Scientific as a model pollutant. Hydrochloric acid (HCl, 37 %), sodium hydroxide (NaOH, 99 %), potassium iodide (KI, 99%), potassium hydroxide (KOH, 85%), hydrogen peroxide (H2O2, 30%) were obtained from Sigma-Aldrich. Iron (III) nitrate nonahydrate (Fe(NO3)3•9H2O, 97 %) was obtained from Merck. All the chemical reagents were used as received. Distilled water was used throughout the study.

2.2. Preparation of Fe3O4, AC and Fe3O4/AC at various weight ratios
AC was synthesised by calcining the sugarcane bagasse at 550°C for 2 h. The AC was then chemically impregnated with Fe2+/Fe3+ aqueous solution prepared by mixing iron (III) nitrate nanohydrate and potassium iodide solution in 3 to 1 weight ratio. The impregnation process was held for 1 h to allow deposition of Fe2+ and Fe3+ ions into Fe3O4 and deposited on AC. Next, the separated solid portion underwent another round of calcination at 550°C for 2 h under nitrogen gas flow to provide inert condition. The calcination process was to enhance the deposition of Fe3O4 onto AC by eliminating the undesired compounds. Fe3O4, AC and Fe3O4/AC at various weight ratios (1:1, 1:3 and 3:1) were synthesised. The corresponding prepared samples are denoted as FeAC11, FeAC13 and FeAC31.

2.3. Sample characterisation
The surface morphology of synthesised samples were observed using Hitachi S-3400N scanning electron microscope which was operated at 20 kV. Elemental analysis was conducted by coupling scanning electron microscope with Hitachi S-3400N energy dispersive X-ray. Crystal phase of the samples were identified using Shimadzu XRD-6000 powder X-ray diffraction. A monochromatised Cu-Kα (λ = 1.5405 Å) radiation course was monitored at 40 kW/3 mA. The 2θ range covered was from 10 to 70° with the scan rate of 2 °/min. Fourier transformed infrared (FTIR) spectra were recorded using a Nicolet IS10 spectrophotometer. The wavenumber covered was in the range of 400 – 4000 cm⁻¹.

2.4. Analysis of liquid samples by undergoing heterogeneous photo Fenton and Fenton-like degradation of malachite green
1 g/L of catalyst was put into 100 mL of 30 ppm malachite green aqueous solution in a beaker. The suspension was stirred using magnetic stirrer throughout the degradation process to ensure a good adsorption/desorption equilibrium between malachite green molecules and the catalyst surface.
Photocatalysis irradiation was conducted by means of a Philip halogen lamp, which acted as energy source (UV intensity of 30 μW/cm²). The sample solution was collected every 5 min for a duration of 30 min. The catalyst was separated from the solution using a Sigma 3-18K centrifugal machine before analysing the remaining concentration of malachite green using a Jenway 6320D UV-vis spectrophotometer. The maximum absorbance value of 624 nm was used for the concentration analysis of malachite green.

3. Results and discussion

3.1. Characterizations of \( \text{Fe}_3\text{O}_4, \text{AC} \) and \( \text{Fe}_3\text{O}_4/\text{AC} \) at various weight ratios

The SEM images of \( \text{Fe}_3\text{O}_4, \text{AC} \) and \( \text{Fe}_3\text{O}_4/\text{AC} \) at various weight ratios are depicted in Figure 1 (a) – (e), respectively. It was observable that \( \text{Fe}_3\text{O}_4 \) displayed fine spherical shape of particle structures and agglomerated together as shown in Figure 1 (a). As reported by Liu et al. [6], the synthesised \( \text{Fe}_3\text{O}_4 \) particles were present in a combination of spherical and square shaped agglomerated grains. On the other hand, \( \text{AC} \) appeared as pieces-like in structure as illustrated in Figure 1 (e). The structure of sugarcane bagasse \( \text{AC} \) is akin to plant tissue structures after subjecting to pyrolysis and activation process [7]. The samples for \( \text{FeAC}31, \text{FeAC}11 \) and \( \text{FeAC}13 \) demonstrated a combined surface morphology for both \( \text{Fe}_3\text{O}_4 \) and \( \text{AC} \) samples due to the samples were prepared by varying the weight ratio between \( \text{Fe}_3\text{O}_4 \) and \( \text{AC} \). For the \( \text{FeAC}31 \) composite sample, the \( \text{Fe}_3\text{O}_4 \) particles tend to be aggregated on the surface of \( \text{AC} \), hence, majority of particles could be observed as shown in Figure 1 (b). \( \text{FeAC}11 \) with 1 to 1 weight ratio between \( \text{Fe}_3\text{O}_4 \) and \( \text{AC} \) was identified to have similar portion of particles and pieces like structure as demonstrated in Figure 1 (c). On the other hand, \( \text{FeAC}13 \) illustrated the pieces-like structure as the majority portion due to high proportion of \( \text{AC} \) to \( \text{Fe}_3\text{O}_4 \) as illustrated in Figure 1 (d).

![Figure 1. SEM images of (a) \( \text{Fe}_3\text{O}_4 \), (b) \( \text{FeAC}31 \), (c) \( \text{FeAC}11 \), (d) \( \text{FeAC}13 \), (e) \( \text{AC} \).](image)

The crystal structure of \( \text{Fe}_3\text{O}_4, \text{AC} \) and \( \text{Fe}_3\text{O}_4/\text{AC} \) at various weight ratios was analysed using XRD analysis. Figure 2 (a) demonstrates the XRD pattern of various composite samples. It was revealed that the peaks appeared at 30.3, 35.7, 43.4, 57.4 and 63° indicated the face-centred cubic structure of \( \text{Fe}_3\text{O}_4 \) [8]. Liu et al. [6] identified that the diffraction peaks appeared at 35.51, 43.13, 53.50, 57.04 and 62.61° symbolised the presence of \( \text{Fe}_3\text{O}_4 \) as the major crystalline phase. From Figure 2 (a), it could be concluded that \( \text{Fe}_3\text{O}_4 \) was found in the sample (a) - (d) as the main diffraction peaks.
were appeared at around 30, 35, 43 and 57°. This results were tally with the literatures. Based on Figure 2 (e), a broad peak around 22° was observed for the sample AC. The peak might be represented the cellulose crystal in the AC [9]. A broad and small peak observed might indicated the cellulose structure was partially or completely burnt off at temperature above 300°C while performing the calcination process under inert environment [10]. AC sample show a broad peak at 2θ = ~23° and a less intense peak at 43° corresponding to the reflection from the amorphous carbon of (0 0 2) and (0 0 1) planes and indicated that the AC consists of graphite-like microcristallites. Other peaks at about 38 and 45° might be corresponded to K related compounds found in the AC derived by KOH activation. Similarly, FeAC13, FeAC11 and FeAC31 which involved the AC as the support material showed a small peak at around 22°, signifying the presence of AC [11]. The appearance of this peak for Fe₃O₄/AC composite samples implied that the Fe₃O₄ was distributed on AC support.

The functional groups of Fe₃O₄, AC and Fe₃O₄/AC at different weight ratios were analysed using FTIR analysis. Figure 2 (b) illustrates the spectra of different composite samples from the range of 500 to 4000 cm⁻¹. The broad peak appeared at 3400 cm⁻¹ for all the synthesised composite samples accounted by the stretching vibration of -OH groups [11]. Similar peak was reported by Rattanachueskul et al. [8], where the stretching vibration of -OH groups occurred at the peak of 3427 cm⁻¹. Another peak at around 2350 cm⁻¹ was observed for FeAC13 and AC samples. The peak indicated the alkyne groups formed as the result of liberating light volatile matters such as hydrogen group during calcination process [12]. A peak observed at about 1087 cm⁻¹ for AC, FeAC11, FeAC13, and FeAC31 composite samples was attributed by C-O-C stretching due to the presence of C and O elements in AC. Tao et al. [13] also reported that the peak at around 1040 cm⁻¹ was ascribed by C-OH stretching which involving the elements of C and O. On the other hand, Fe₃O₄, FeAC11, FeAC13 and FeAC31 which consist of iron precursor showed a peak at approximately 560 cm⁻¹. The peak could be ascribed by the stretching of Fe-O [11].

**Figure 2.** (a) XRD patterns (b) FTIR spectra of the synthesized samples.

3.2. Degradation efficiencies of malachite green under various conditions

The effect of various type of catalysts such as Fe₃O₄, AC and Fe₃O₄/AC at different weight ratios (3:1, 1:1, 1:3) on the heterogeneous photo Fenton and Fenton-like degradation of malachite green was studied and shown in Figure 3 (a). It was observable that with photo Fenton and Fenton-like degradation of malachite green in the presence of AC could only achieved 18.43 %. It showed lower degradation efficiency than Fe₃O₄, and Fe₃O₄/AC during heterogeneous photo Fenton and Fenton-like degradation.

Similar finding was reported by [11], where the iron oxide catalysts had higher degradation efficiency of phenol than pure AC catalyst. As depicted in Figure 3 (a), a lower degradation efficiency of malachite green in the presence of Fe₃O₄ was observed as compared to FeAC13, FeAC31 and FeAC11. The degradation efficiency of malachite green for Fe₃O₄, FeAC13, FeAC31 and FeAC11 was 30.26, 73.00, 76.33 and 86.84 %, respectively. It was anticipated that a combination of adsorption
and heterogeneous photo Fenton and Fenton-like degradation were happened in the presence of catalyst. Among three different weight ratios of Fe\textsubscript{3}O\textsubscript{4} to AC, FeAC\textsubscript{13} showed a lower degradation efficiency than FeAC\textsubscript{11} and FeAC\textsubscript{31}. It was deduced that AC was not evenly covered by Fe\textsubscript{3}O\textsubscript{4} due to the excessive amount of AC present in FeAC\textsubscript{13}. Messele et al. [14] revealed that lower Fe/AC weight percent led to a decrement of phenol removal rate. On the other hand, FeAC\textsubscript{31} demonstrated a lower degradation efficiency as compared to FeAC\textsubscript{11}. This could be attributed by the excessive amount of Fe\textsubscript{3}O\textsubscript{4} distributed on AC, causing the blockage of meso or microporous sites on the AC [15]. FeAC\textsubscript{11} with optimum weight ratio of Fe\textsubscript{3}O\textsubscript{4} and AC which possesses the highest degradation efficiency of malachite green was then used for the subsequent study.

![Figure 3](image)

**Figure 3.** Effects of (a) various types of catalysts (b) catalyst dosage (c) solution pH (d) H\textsubscript{2}O\textsubscript{2} amount on the heterogeneous photo Fenton and Fenton-like degradation efficiency of malachite green.

The effect of catalyst dosage (0, 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 g/L) on the heterogeneous photo Fenton and Fenton-like degradation of malachite green was studied. The results are depicted in Figure 3(b). The degradation efficiency of malachite green was merely 1.9% in the absence of FeAC\textsubscript{11} composite sample. This indicated that photolysis could only contribute extremely low degradation efficiency of malachite green. [16] reported similar outcome where the photolytic degradation efficiency of dyes was much lower as compared to photocatalysis and photoelectrocatalysis. The degradation efficiency was increased from 44.47% to 87% with the increment of catalyst dosage from 0.2 to 0.8 g/L. A greater amount of active sites were available on the catalyst surface upon increasing the catalyst dosage. Besides, the generation of hydroxyl radical was enhanced with the increasing of active sites. These factors accelerated the degradation process and improved the overall degradation efficiency [17]. Nonetheless, the degradation efficiency experienced a small drop from 87.39 to 86.84 and 86.83% if further increasing the catalyst dosage from 0.8 to 1.0 and 1.2 g/L, respectively. Excessive amount of catalyst might inhibit the light penetration in the dye solution, decreasing the number of photons absorbed by the particles. Consequently, less amount of •OH radicals would be generated [18]. Hence, the optimal catalyst dosage was fixed at 0.8 g/L as it
generated the highest degradation efficiency. The optimal catalyst dosage was used for following parameter studies.

The effect of solution pH on the heterogeneous photo Fenton and Fenton-like degradation of malachite green was identified. The solution pH was varied in the range of pH 1, 3, 5, 7 and 9 with the aid of 0.1 M NaOH and 0.1 M HCl to adjust the pH value. The outcome of the experiment is illustrated in Figure 3(c). The degradation efficiency was enhanced dramatically from 34.03 to 88.43% when adjusting the pH from 1 to 5 before a plateau point reached at 88 % upon further increasing the solution pH to 7 or 9. The lowest degradation efficiency at pH 1 was ascribed by the weak interaction between malachite green and catalyst surface in acidic environment. Malachite green is a cationic dye which might experience a repulsive force with the positively charged catalyst surface as the result of protonation effect. In addition, there could be a competition between positively charged ions such as H+ and dye molecules for the same binding site on the catalyst surface in acidic solution [19]. As discussed [19], low amount of malachite green adsorbed on the positively charged catalyst surface due to the occurrence of H+ ions that would compete for the active site on the catalyst. The improvement in degradation dye performance at higher solution pH value was mostly related to the different charges between dyes molecules and catalyst surface. When the solution was approaching neutral or alkaline condition, the surface of the catalyst tends to be more negatively charged due to the accumulation of OH− ions produced at high solution pH. Subsequently, a strong electrostatic force formed between the OH− ions on the catalyst surface and the cationic dyes, leading to a better degradation efficiency. Similar trend was reported by [20], where the degradation efficiency increased from pH 2 to around pH 6 before levelling out at higher pH value. Optimal pH was identified at pH 5 and was used for further parameter studies.

The effect of H2O2 dosage (0, 1, 2, 3, 4, 5 and 6 mM) on the heterogeneous photo Fenton and Fenton-like degradation efficiency of malachite green was analysed and the results are shown in Figure 3 (d). It was notable that the degradation efficiency was increased from 14.53 to 89.22 % when increasing the H2O2 dosage from 0 to 4 mM, respectively. The degradation efficiency was enhanced with larger amount of H2O2 supplied due to the growing amount of •OH radicals produced [21]. [22] acquired the similar upward trend where the degradation efficiency raised when the H2O2 dosage was increased from 5 to 7.4 mM as the result of escalating the number of •OH radicals yielded. Degradation efficiency was dropped slightly to 88.85 and 87.96% upon increment of H2O2 dosage to 5 and 6 mM, respectively. This indicated that the increment of degradation efficiency was halted when exceeding 4 mM of H2O2. The situation could be explained by the scavenging effect of excessive H2O2 that could lead to the production of HO2• radicals, which had lower reactivity than •OH radicals [23]. According to the study conducted by [24], resembling scenario was encountered where the degradation efficiency raised upon increasing the H2O2 dosage from 1500 to 2000 mg/L before a deceleration at the dosage above 3000 mg/L. Hence, the optimal dosage for H2O2 was selected at 4 mM in this study. This value was used for following study.

3.3. ICP-OES study
To ensure the catalyst function consistently for a long period, stability of a catalyst is desirable. The degradation efficiency of the catalyst might be reduced as the result of leaching. It was reported that the degradation efficiency of phenol dropped to 75% after 4 repetitive runs and the situation could be attributed by leaching of metal from the catalyst [11]. Thus, it is important to study the stability of catalysts with the aid of ICP-OES where the concentration of dissolved iron in the final solution after 3 min reaction under optimum condition was determined. Department of Environment had stipulated the acceptable condition for discharge of industrial effluent of Standard B in which the maximum allowable concentration of Fe is below 5 mg/L [25]. The concentration of leached iron detected in the final solution on heterogeneous photo Fenton and Fenton-like degradation of malachite green was plotted in Figure 4. Based on ICP-OES results, the concentration of leached iron in the final solution was 4 mg/L. The concentration of leached iron could be considered relatively low as the values were in the acceptable range for discharge of iron (less than 5 mg/L).
4. Conclusions

Fe$_3$O$_4$, AC and Fe$_3$O$_4$/AC composite samples at various weight ratios were successfully synthesised by chemical impregnation, followed by calcination under inert environment at 550 °C for 2 hours. All the synthesised samples were then characterised by using SEM-EDX, XRD and FTIR. SEM depicted that Fe$_3$O$_4$ was spherical and square shaped agglomerated grains whilst the AC was pieces-like in structure. In addition, Fe$_3$O$_4$/AC composite samples at various weight ratios showed a combination of irregular shapes and pieces-like structures. EDX demonstrated that the amount of Fe and C elements increased upon raising the weight ratio of Fe$_3$O$_4$ and AC in the composite samples. Moreover, the atomic ratio of Fe and O for Fe$_3$O$_4$ was approximately 3 to 4. On the other hand, FTIR analysis indicated that several functional groups such as O-H, C≡C and C-O-C bonding were present in samples possessing AC. Furthermore, Fe-O stretching at 570 cm$^{-1}$ indicated the presence of Fe$_3$O$_4$. Among the composite samples synthesised, FeAC11 showed the highest degradation activity due to its appropriate amount of Fe$_3$O$_4$ present in AC and caused less blockage of active site. The optimum conditions for degrading malachite green were acquired at initial dye concentration of 30 ppm, FeAC11 dosage of 0.8 g/L, pH 5, H$_2$O$_2$ dosage of 4 mM with the degradation efficiency of 89.22 % after 3 min of reaction time. Besides, ICP-OES results demonstrated that the synthesised composite sample (FeAC11) had high stability as only small amount of leached iron (about 4 mg/L) detected in the treated solution. The reaction kinetics of heterogeneous photo Fenton and Fenton-like degradation of malachite green at various solution pH were followed pseudo second-order kinetics.

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