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Iron Oxide Nanoparticles Derived from Mill Scale Waste as Potential Scavenging Agent in Dye Wastewater Treatment for Batik Industry

Azdiya Suhada Abdul Rahim Arifin[1,a*], Ismayadi Ismail[1,b], Abdul Halim Abdullah[2,c], Farah Nabilah Shafiee[1,d], Rodziah Nazlan[1,e] and Idza Riati Ibrahim[1,f]

[1]Materials Synthesis and Characterization Laboratory, Institute of Advanced Technology (ITMA), Universiti Putra Malaysia,43400 Serdang, Selangor, Malaysia

[2]Department of Physics, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

[a]azdiyasuhada.abdrahim@gmail.com, [b]ismayadi@upm.edu.my, [c]halim@upm.edu.my, [d]farahnabilahshafiee@gmail.com, [e]rodzienaz@gmail.com, [f]idza411@gmail.com

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Abstract. In this work, iron oxide were derived from millscale has been used as a potential scavenging agent in wastewater treatment due to its high adsorption capacity and its shorter sedimentation time during wastewater treatment. Iron oxide obtained from the magnetic separation technique was subjected to high energy ball milling (HEBM) at different milling time to produce different size of nanoparticles of iron oxide. X-ray diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM) and Scanning Trasmission Electron microscopy (STEM) were performed to study the morphological properties of the iron oxide nanoparticles. After HEBM, iron oxide nanoparticles were modified with Hexadecyltrimethylammonium Bromide (CTAB) to study the adsorption possibility of iron oxide nanoparticle modified with CTAB (Iron oxide– CTAB nanoparticles) in dye wastewater. The variation effect of particle size of derived Iron oxide– CTAB were studied. Permanent magnet was used to separate iron oxide nanoparticles from the solution. The clear part of the solution (treated wastewater) was filtered out and adsorption efficiency of Iron oxide– CTAB nanoparticles was measured using UV – Visible spectroscopy. Efficiency adsorption of iron oxide nanoparticles modified with CTAB greatly achieved above 99 % and the size of iron oxide nanoparticles was found to be affecting its performance in dye wastewater treatment.

Introduction

Nowadays batik factories are developing coherently with other textile factories and batik textile has become a trend among the society in Malaysia. However, during batik fabrication process the use of tremendous amount of clean water and disposal of wastewater from batik industries into the water bodies such as rivers, lakes and oceans is very alarming. The wastewater contains chemical substances such as dyes, sodium silicate, sodium alginate and sodium salt [1]. When the wastewater is discharged into the water bodies, the aquatic life and human health is threatened due to the complex and poor biodegradable of dye [2]. For example intestinal cancer, cerebral abnormalities in the fetus and skin allergy are some kind of diseases which may be risky to the human health [3]. Hence, the removal of the substances in the batik wastewater becomes a crucial challenge for human diversity. Many techniques were employed to scrutinize the dye removal from wastewater including coagulation/flocculation [4], membrane separation [5-6], photodegradation [7-8] and adsorption techniques [9-10]. Among these techniques, adsorption technique using iron oxide nanoparticles has been discovered as the most effective, low cost, capable in treating azo contain in wastewater and reusable adsorbent [11]. Instead of focusing on the application of iron oxide nanoparticles as dampening and cooling agents in loudspeaker [12-13], drug release [14] and ferrofluids [15], researchers also attempted utilizing the iron oxide nanoparticles as an adsorbent due to the special unique properties of iron oxide with small nanoparticles size, very large surface area and surface modification which exhibited high adsorption capacity [16]. Apart from that, iron oxide nanoparticles are easily get separated from the solution under an applied external magnetic field resulting in shorter sedimentation time of iron oxide nanoparticles during wastewater treatment [17]. Thus, iron oxide nanoparticles are potentially used as an adsorbent for dye removal in the batik wastewater treatment. This present study aimed to investigate the particle size effect of iron oxide – CTAB nanoparticles on the adsorption efficiency in the batik wastewater treatment. In this work, batik wastewater was collected from Masterwan Batik Factory at Dengkil, Selangor.

Materials and Methods

Iron oxide was extracted from mill scale using the magnetic separation technique (MST) to separate iron oxide particles from non–magnetic particles and other impurities. Iron oxide obtained was mixed and crushed into smaller particles using conventional milling for 12 hours before preceded to High Energy Ball Milling (HEBM). 10 grams of iron oxide powder was milled via SPEX8000D HEBM machine using a ball-to-powder-weight ratio of 10:1 at room temperature in various milling time of 4, 6, 12 hours to obtain different iron oxide nanoparticles sizes. Resultant iron oxide nanoparticles powder was then modified with CTAB to reduce aggregation of iron oxide nanoparticles and provide interaction between adsorbent and particles in the batik wastewater [18-19]. 0.5 g of CTAB powder was then completely dissolved in 40 ml of distilled water before 4 g of iron oxide nanoparticles being added into the solution. The solution was mixed for 30 minutes at 3000 rpm by using a Mini Vortex Mixer. Later, the solution was filtered, rinsed with deionized water for several times and left dried in oven at 65 ^{0}C. Later on, 4 g of Iron oxide–CTAB nanoparticles were added into 150 ml of batik wastewater. The solution was then mixed at 3000 rpm for 60 minutes. Then, an external magnetic field was applied to separate the Iron oxide–CTAB nanoparticles from the batik wastewater. Extraction time was fixed at 30 minutes. Iron oxide phase was confirmed with an X-ray diffraction (XRD). Microstructural study and particles size of iron oxide was studied using a FESEM and STEM respectively. UV–Vis spectroscopy was used to study the effect of iron oxide nanoparticles size variation on the performance of adsorption process of Iron oxide–CTAB nanoparticles in the batik wastewater.

Results and Discussion

Microstructural Studies

Figure 1 shows multi–plot sets of XRD spectra of iron oxide nanoparticles at various milling time of 4, 6 and 12 hours by using an X'Pert PANalytical diffractometer (PW3050/60) and CuKα radiation source in a range of 2θ from 20^o to 80^o. Clearly observed that, sharp narrow peaks (Figure 1) emerged for iron oxide sample before undergoes HEBM process indicated highly crystalline structure of iron oxide particles were successfully extracted from the mill scale using the Magnetic Separation Technique. Iron oxide consists of magnetite, wuestite and hematite were found and denoted as square, stars and triangle shape respectively in the figure 1. XRD result shows that the milling time affect the peaks profile of the iron oxide. As the milling time increased to 4, 6 and 12 hours, the original sharp peak of iron oxide nanoparticle broadened and overlapped with neighbouring peaks, showing that the iron oxides nanoparticles become more amorphous as the milling time were increased. HEBM process involves flattening, fracturing and welding of the particles repeatedly after collided and trapped between the steel balls in the vials. High energetic compressed force impacted and crushed the particles into smaller particles with high amount of defects, lattice strains and atom dislocations [20].

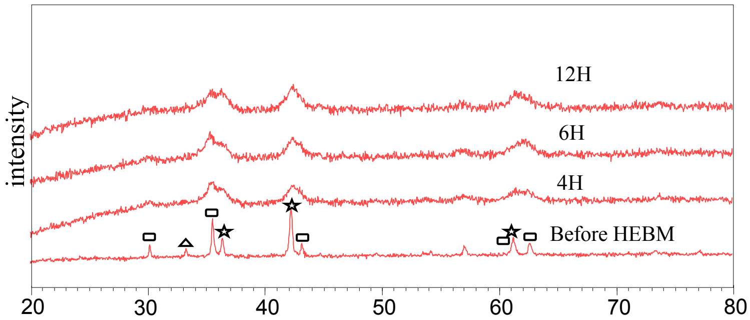


Figure 1. XRD spectra of iron oxide nanoparticles before HEBM and after milling at 4, 6 and 12 hours. ▭ is for magnetite, △ is for hematite and ☆ is for wuestite.

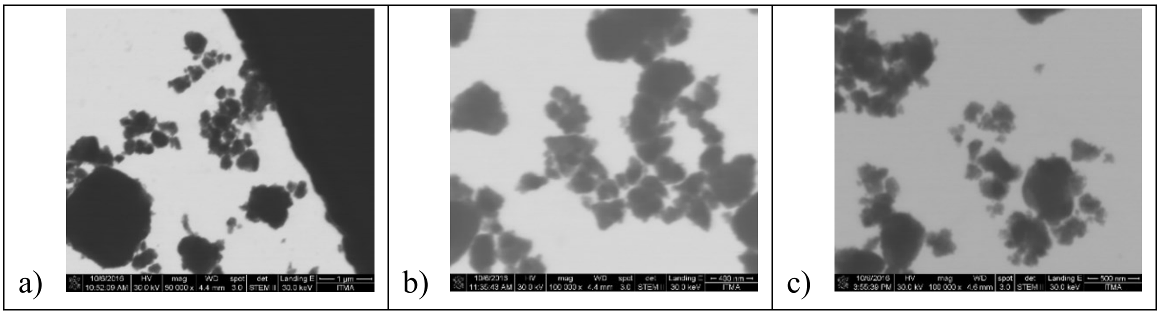
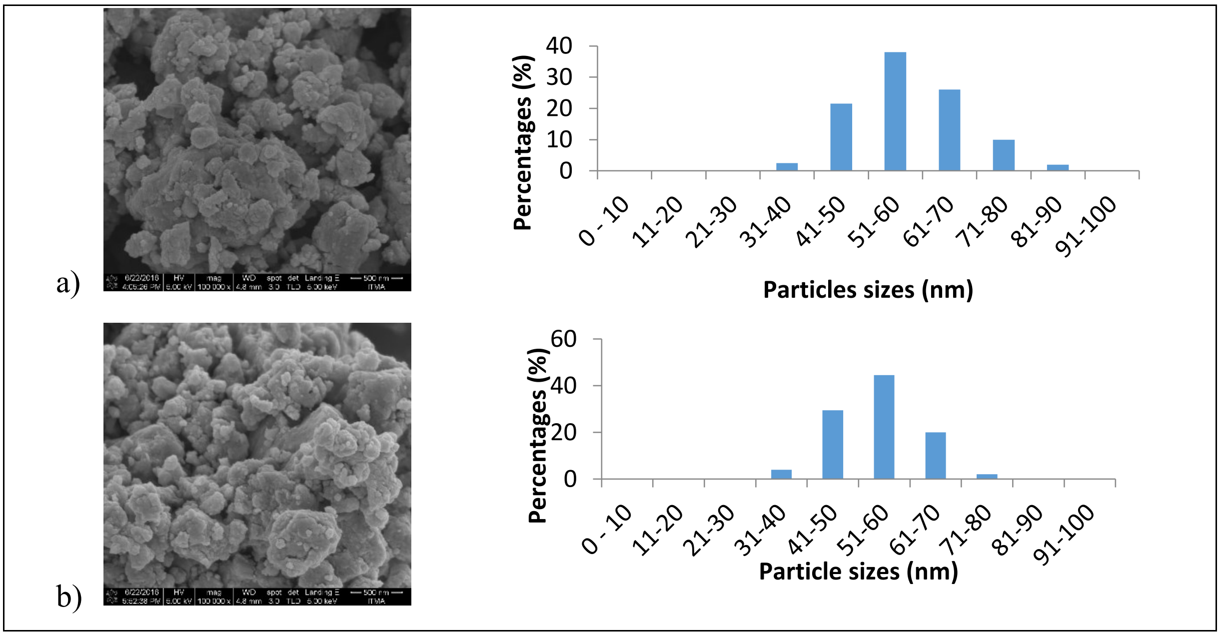


Figure 2. STEM micrograph of milled iron oxide nanoparticles at various milling time a) 4 hours, b) 6 hours, and c) 12 hours.

Figure 2 shows STEM micrograph of iron oxide. The average particle size of iron oxide milled at 4, 6 and 12 hours obtained were 57.02 nm, 53.76 nm and 33.83 nm respectively. The size of iron oxide nanoparticles decreased as the milling time increased due to high energy imparted from the collision of milling media to the iron oxide particles which indicated the increased of the defect density of iron oxide [21]. Figure 3 shows FESEM micrograph and particle size distribution plots of iron oxide nanoparticles at various milling time of 4, 6 and 12 hours respectively. Iron oxide nanoparticles were seen as irregular shapes with high aggregations formed due to the van der Waals force between the particles [22]. The average nanoparticle size of iron oxide for 4 and 6 hours milling time were in the range from 51 to 60 nm, whereas average nanoparticle size of iron oxide milled for 12 hours was in the range of from 21 to 30 nm.



c)

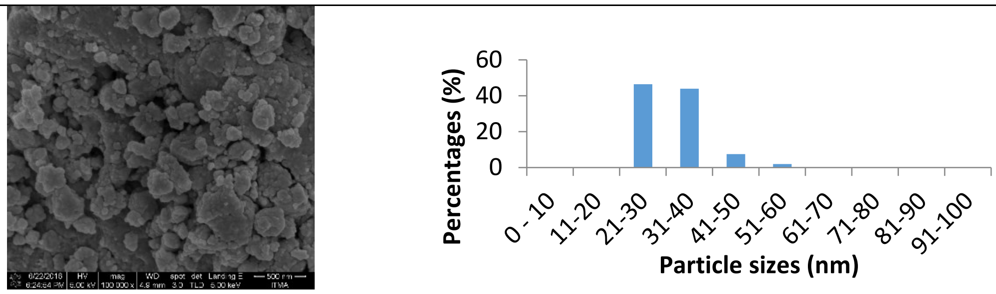


Figure 3. Micrograph FESEM of iron oxide and their particle size distributions at various milling time of a) 4 hours, b) 6 hours and c) 12 hours respectively.

Adsorption Studies

Table 1. Particle size effect of iron oxide nanoparticles on dye removal percentages in batik wastewater.

Particle size (nm)	Percentage of dye removal (%)
57.02 nm	99.90
53.76 nm	99.93
33.83 nm	99.88

Adsorption studies of iron oxide modified with CTAB in the batik wastewater were carried out in a beaker with constant stirring at 3000 rpm for 60 minutes and 30 minutes extraction time of Iron oxide– CTAB nanoparticles from the treated batik wastewater. Calibration curve from UV–Vis data was examined and the percentage of dye removal was calculated and tabulated in Table 1. The efficiency adsorption of Iron oxide–CTAB nanoparticles was based on the percentage of dye removal in the batik wastewater. The maximum peak for absorbance changes of batik wastewater was at 503 nm. Iron oxide–CTAB nanoparticles astonishingly achieved above 99 % percentages of dye removal in batik wastewater (Table 1). Iron oxide nanoparticles having size of 57.02 nm, amazingly removed 99.90% of dye from the batik wastewater and 53.76 nm nanoparticle size of iron oxide successfully removed 99.93% of dye in batik wastewater. The dye removal percentages were increased as the iron oxide nanoparticles were smaller. The results obtained were expected because smaller size of iron oxide nanoparticle provided larger surface area per volume and exhibited an increase of adsorption capacity of iron oxide nanoparticles [23]. However 33.83 nm nanoparticle size of iron oxide shows the percentage of dye removal which was decreased to 99.88%. This might be due to the insufficient energy of extremely small iron oxide nanoparticles to overcome the intense surface energy of the batik wastewater and caused the iron oxide nanoparticles suspended on the surface of the batik wastewater [24]. Hence, the amount of iron oxide nanoparticles contacted with the substances in the batik wastewater was reduced, thus leading to the decreases in percentages of dye removal in the batik wastewater.

Conclusion

Highly crystalline iron oxide particles were extracted from mill scale through Magnetic Separation Technique and was found to be formed highly amorphous iron oxide nanoparticles via high energy ball milling technique at various milling time of 4, 6 and 12 hours. As the milling time increased to 4, 6 and 12 hours, the size of iron oxide nanoparticles were decreased to 57.02, 53.76 and 33.83 nm respectively. Small size of iron oxide nanoparticles provided large surface area per volume and exhibited high efficiency adsorption of iron oxide nanoparticles. Iron oxide nanoparticles were modified with CTAB to reduce aggregation and allow interaction between the adsorbent and particles in the wastewater. Adsorption efficiency of iron oxide nanoparticles modified with CTAB achieved above 99 % and was found to be affected by the size of iron oxide nanoparticles, having the optimum adsorption of 99.93% for sample having particle size of 53.76 nm.

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