ISSN: 2230-9926

Available online at http://www.journalijdr.com

IJDR

International Journal of Development Research
Vol. 5, Issue, 02, pp. 3496-3501, February, 2015

International Journal of
DEVELOPMENT RESEARCH

Full Length Research Article

SYNTHESIS OF DISPERSED NANO ZERO VALENTE IRON WITH DIFFERENT STABILIZERS USING K-MREACTOR

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ARTICLE INFO

Article History:
Received 23rd November, 2014
Received in revised form
04th December, 2014
Accepted 20th January, 2015
Published online 27th February, 2015

Key words:
NZVI,
K-M Reactor,
Stabilizing agents

ABSTRACT

this study, Nano Zero Valente Iron (NZVI) was produced with different stabilizers (Sodiumcarboxymethylcellulose, CMC, Polyvinylpyrrolidone, PVP, Hexadecyltrimethylammonium bromide, CTAB using kinetic energy micro reactor (K-M reactor). There action between Ferric chloride ($FeCl_3.6H_2O$) with different stabilizers and Sodium borohydriede ($NaBH_4$) as reducing agent at K-M reactor gives many advantages in comparison with traditional chemical method for production of dispersed Nano ironin batch reactor. The produced Nano iron using micro reactor showed better characteristics than those produced using batch reactor in different aspects such as homogeneity of the produced particles, particle size distribution and stability. The results showed that Fe-CTAB is highly dispersed with time more than 3 hr according to Visual and optical in spectional so the shape of Fe-CTAB is spherical and give smallest Nano size in comparison with Fe-CMC and Fe-PVP. Different techniques were used for investigation and characterization of the produced dispersed Nano iron particles such as UV-Vis, TEM and PSD.

INTRODUCATION

NZVI agglomeration results from vander Waals and magnetic particle-to-particle attractive forces (He and Zhao, 2005 and Liu *et al*., 2007) and shown in Fig.1. To prevent particle aggregation a wide variety of stabilizers have been proposed to modifyn ZVI particle surface characteristics. Mechanisms that are commonly exploited to improve particle stability in aqueous suspensions include stericandel ectrostatic hindrance. Sterichindrance occurs when largesize stabilizers adsorbon the particle, creating bulky moieties on the particle surface. These moieties preventinte rparticle interactions by counteracting particle–particle attractive forces which results in limited particle aggregation. Electro static hindrance occurs through an increase in particle net surface charge, leadingto repulsive interactions between particles of similar charge. Stabilizers have been used to modify the surface of nZVI particles during (pre- synthesis addition of stabilizer) and following (Post-synthesis addition of stabilizer) iron nanoparticle synthesis (Sakulchaicharoen *et al*., 2010). In this work, nZVI are synthesized using PVP, CTAB, and CMC using are reduction process synthesis for Nanoiron and addition approach to compare the stability and reactivity of these modified Fe nano particles. Although PVP stabilizers have been studied extensively successfully (Nagasaw *et al*., 2005), and also CMC stabilizers (He and Zhao, 2005 and Nagasaw *et al*., 2005). But the different in this contribution presents a study is the first time it has been used for nZVI synthesis advanced technic of micro reactor technologies also study the effect of CTAB stabilizers for Nanoiron, it's anew and this study open anew reaches about solving the agglomeration problem of Nanoiron by using advanced materials and technics.

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Research ork

K-M reactor

As shown in Fig.2, K-M reactor consists of three stainless steel plates, that is, the inlet, the mixing and the out let cylindrical plate.

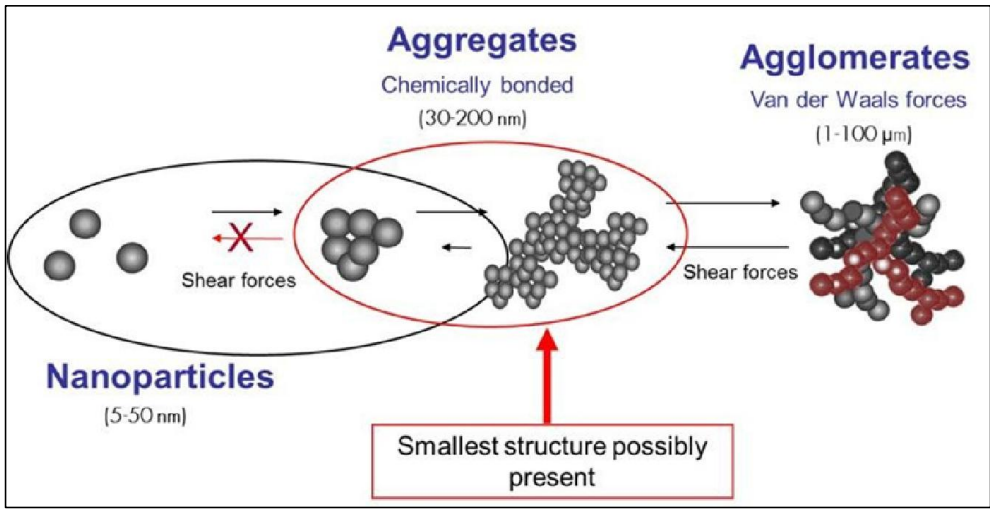
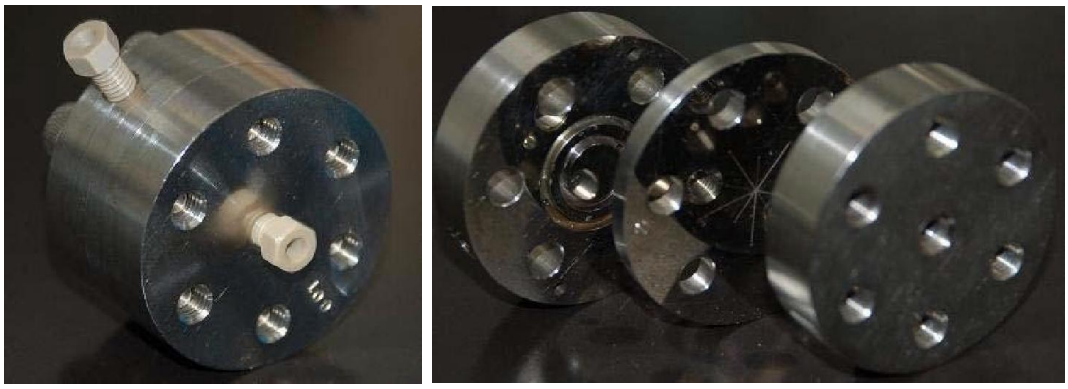
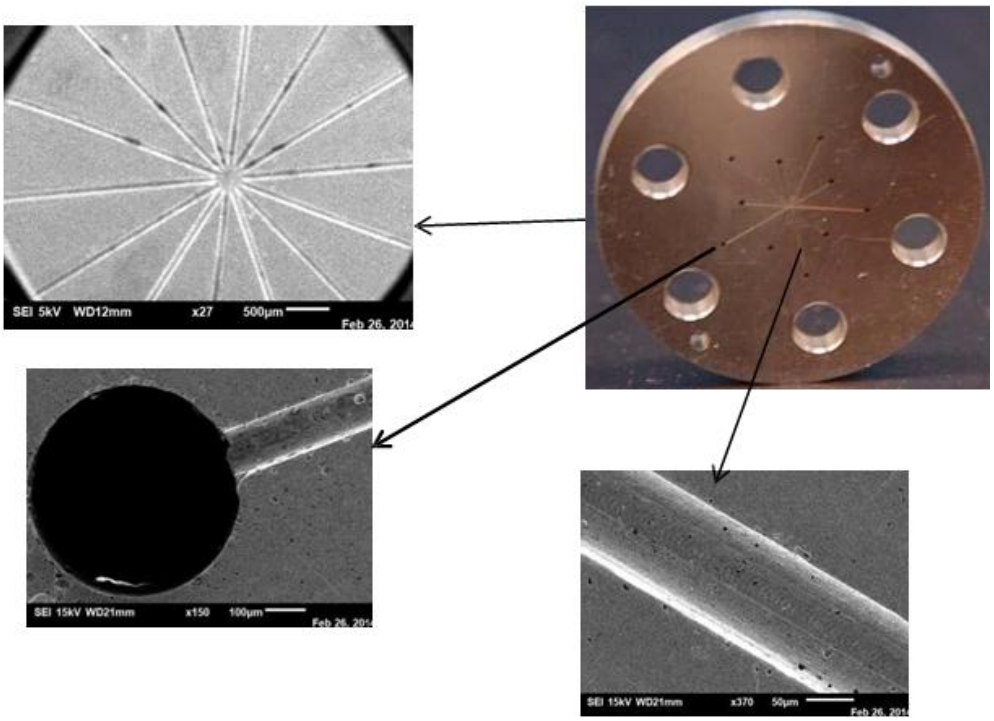


Fig.1. Agglomeration of nanoparticles



(a) Over view (b) Exploded view



(c) Mixingplate

Fig.2. K-Mreactorparts

On each plate, some of the channels were fabricated mechanically to form fluid streams and each of these surfaces was planished precisely for sealing by metal touch. These plates were arranged face to face and tightened with the same torque by six screws to prevent leakage from the metal touch seal. The details of the internal structure and stream lines in the micro mixer are summarized as follows: on the inlet plate, the annul archannels, which had a square section of 1.5 mm, were connected to the two inlets for two different fluids. The annular channels play a role in uniformly feeding two fluids in to the inlets of the micro channels on the mixing plate. On the mixing plate, micro channels with asquare cross section were fabricated in the radial by Micro Electric Discharge Machining (μ- EDM). The number of micro channels was determined from the layout of the channel on the plate for each channel width was found to be 14. The stream of each fluid was divided in to half of the total number of micro channels. The two divided fluids meet at the center of the mixing plate and immediately mixed. The diameter of the mixing zone was found to be 220μm. The depth of the mixing zone corresponded to the micro channel depth. At that point, thevelocity of the mixed fluidis equal to the velocity of each micro channel when the flow rates of the two fluids are the same. Finally, the out let plate has a hole for the exit of the mixed fluid at the center of the plate, the exithole (200μm) which is smaller than the diameter of the mixing zone to accelerate the mixing process (Yuvakkumara *et al.,* 2011).

Mixing Experiments

The iron nano particles were synthesized at K-M reactor in ethanol medium as shown in Figs. 2, based on the following reaction

$$2FeCl_3+6NaBH_4+18H_2O \longrightarrow 2Fe^0+6NaCl+6B(OH)_3+21H_2$$

(Doson *et al*., 2000)

For production of Nano iron with different stabilizers by using K-M reactor most important variable such stability of Nano iron was investigated.The produced solid particles were washed three times with 25ml portions of absolute ethanol to remove all of the water and prevent the rapid oxidation of the produced nano iron particles. The synthesized nano particles were finally dried in vacuumovenat 70^oC overnight.

MATERIALS AND METHODS

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, Sigma Aldrich), sodium borohydride ($NaBH_4$, Sigma Aldrich), sodiumcarboxymethyl cellulose, CMC, M_W=90,000, polyvinylpyrrolidone PVP,M_W=10000, hexadecyltrimethylam moniumbromide, CTAB, Sigma Aldrich) and absolute ethanol will beused beside deionized water for all system.

Experimental work

Each of PVP (0.02M), NaCMC (0.002M) and CTAB (0.02M) mixed with $FeCl3.6H_2O$ by volume 10:10, at constant concentration of $FeCl3.6H_2O$ (0.02M) in 20ml of deionized water and constant concentration of $NaBH_4$ (0.06M) in 20ml of deionized water at constant flow rate of 10 ml/min were mixed in a K-Mreactor. The black colored particles were washed trice with absolute ethanol and finally separated by magnet, dried, and storage.

Physical characterization

NZVI with stabilizers were characterized for dispersion stability by visual inspection of settling behavior (taking pictures at specific times to monitor the settling process). To perform this, after nZVI synthesis, part of the nano particle suspension was transferred into 50mL bottle. The stability of the nano particle suspension was evaluated by taking photographs of undisturbed nZVI suspensions every 30min for 3hr. The pictures for each nZVI formulation were then compared. TEM analysis was performed using a JOEL1010 Transmission Electron Microscope. The samples were prepared by dropping 1 drop of fershly synthesized nano particles on copper grid. The samples were then dried in oven under avacuum. Micrographs were obtained on each sample, and the diameter of each particle on those micrographs was measured in order to obtain diameter distributions. The samples were prepared by separation of Nano iron by magnet and washing by ethanol for more times and thin dried in oven under vacuum. UV-vis multispecies (Shimadzu, Ltd., Multispec-1500) will be used for determine sedimentation of Nano iron with time at the same concentrations of stabilizer s and volume 2ml for each cuvette by monitoring the optical absorbance at 508nm as a function of time. All measurements were made after 1hr. for each samples under super sonication and time = 3hr. under UV-vis.

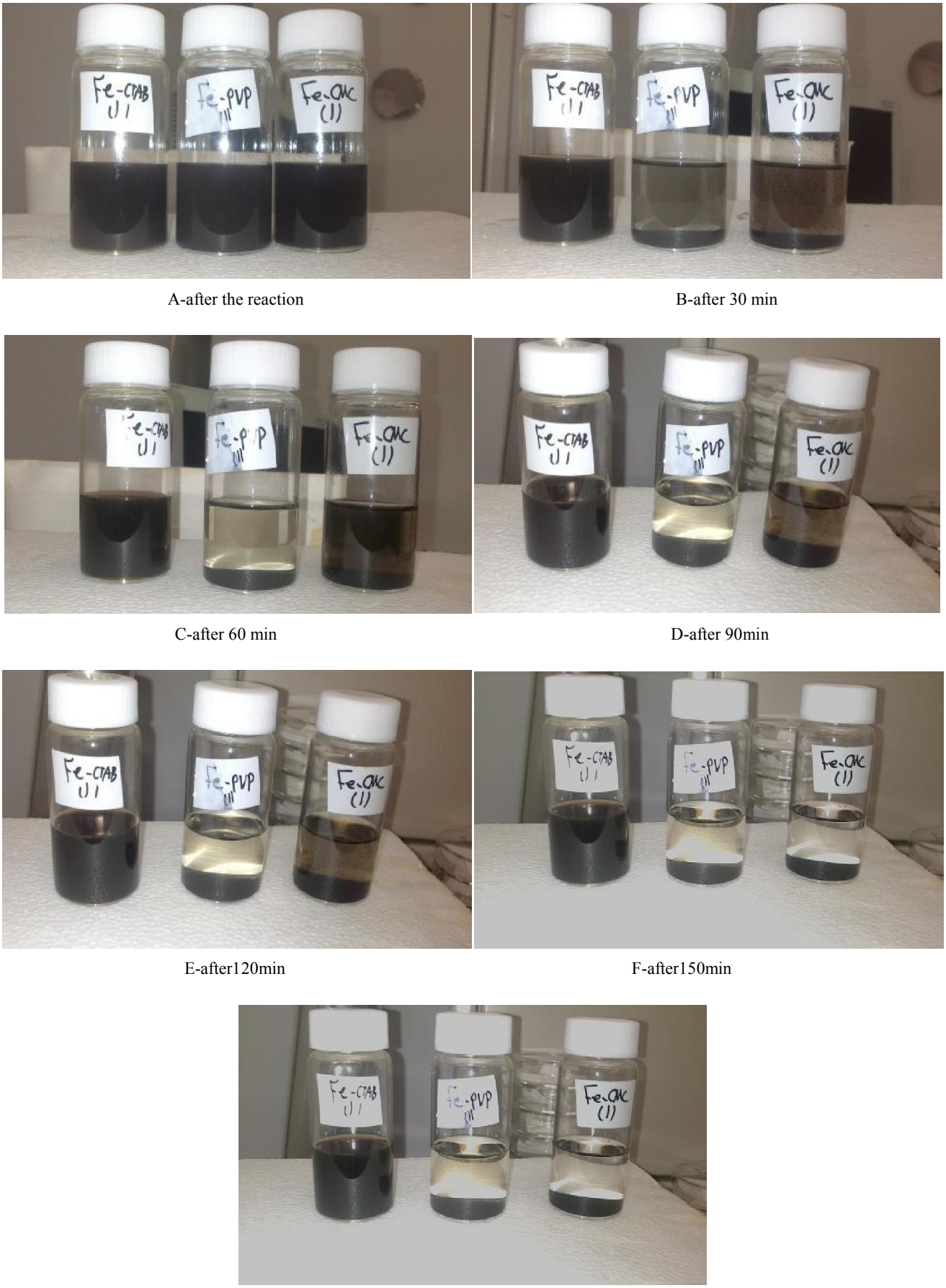
Stability tests

The stability of Fe nano particles is shown in Fig. 3 A,B,C,D.E,F and G). Both the CTAB yielded stable Fe nano particle suspensions in excess of 3 h and CMC at 2h (Fig. 3 G and E) where as PVP did not result in stable nano particle suspensions for an extended period (Fig.3C). Sedimentation curves (Fig.4 are in good agreement with visual observations (Fig.4. CTAB yields the most stable suspension with a stability time of 3 h (i.e., time required to achieve an absorption intensity that is 50% of the initial intensity (Sakulchaicharoen *et al*., 2010) (I/Io= 0.5)). Nano particles stabilized with CTAB yielded similar sedimentation curves, with stability times of 3h. Nano particles stabilized with PVP were less stable than CMC (stability time of 20 min) how ever CMC performed much better than PVP and bare nano particles which settled out of solution in one hour.

RESULTS AND DISCUSSION

TEM and diameter distribution

TEM micrographs for stabilized Fe nano particles, using the K-M reactor, are shown in Fig.5. The diameter distributions obtained for each sample are shown in Fig.6. CTAB is cation - ic surfactant that has strong positive charge and can be strongly absorbed on to the iron nano particle surface via its head group and contains a hydro phobic saturated hydro carbon tail attached to a charged head group as shown Fig.7A



A-after the reaction

B-after 30 min

C-after 60 min

D-after 90min

E-after120min

F-after150min

G-after180min

Fig.3.Visual inspection of Nano iron with stabilizers at different time

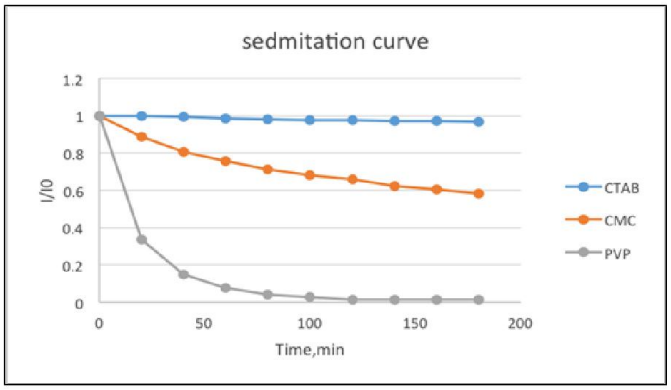
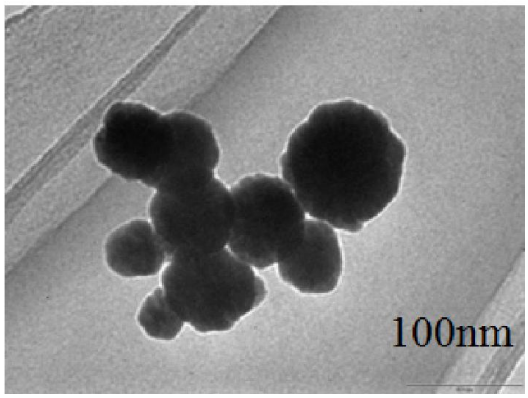
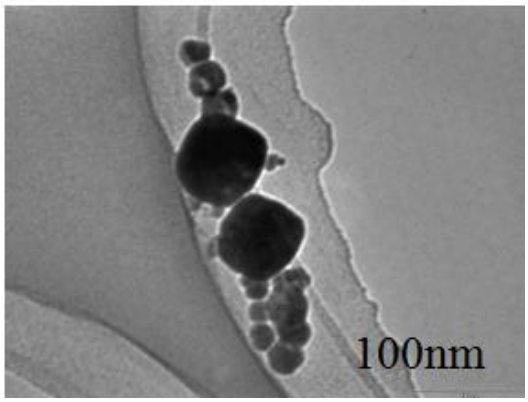


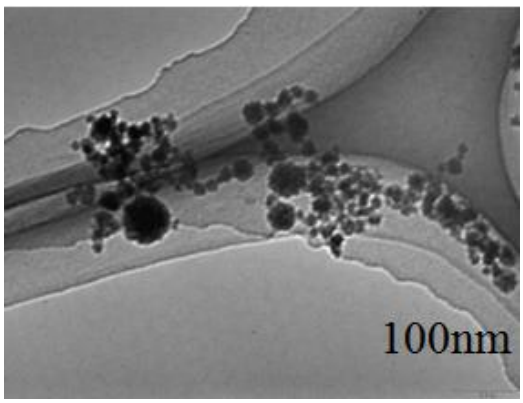
Fig.4. Sedmentation curve of Nano iron with different stabilizer



a



b



c

Fig.5. TEM images of Nanoiron with (A-PVP, B-CMC and C- CTAB)

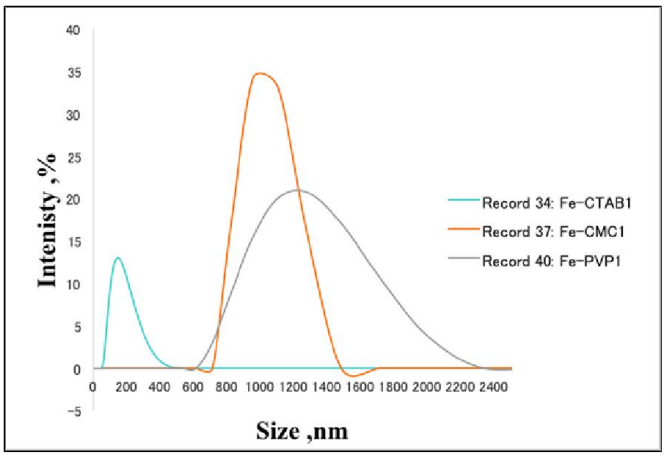
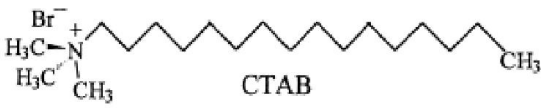
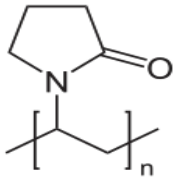


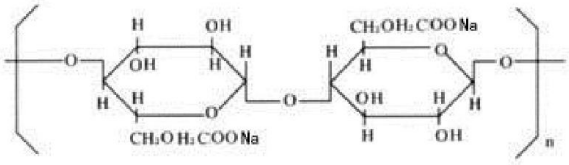
Fig.6. Particle size analyzer of Nano iron with CTAB, CMC and PVP



A



B



C

Fig.7. Chemical structure of A-CTAB, B-PVP and C-CMC

(Doson *et al* ., 2000). The positive charge on the CTAB head group is embedded in a hydrocarbon shell and hydrophobic interactions are expected to play a greater role in adsorption of CTAB on surface of Nano iron (Doson *et al*., 2000). It is a good dispersion and protection layer for their on nanoparticles preventing the oxidation of iron during its passivation and storage. This is in agreement with increased sterich indrance that results when CTAB molecules are used during synthesis. CTAB, with a net Positive charge, limits nanoparticle growth in comparison to the other neutrally charged stabilizers (i.e., PVP) who seuse result edinlarger nanoparticles. In the case of PVP there are two important differences when compared to CTAB and CMC. The first is that Fe^{3+}ions likely form weak bonds with the lonepair electrons at the oxygenatom on the PVP carbonyl group. The interaction between PVP and Fe3+(i.e., lone pairelectrons and Fe^{3+}) is weak erthan CTAB–Fe^{3+} interactions and CTAB-Fe3+ (i.e., Fe^{3+}/–COO- and Fe3+/Br—N+-CH3-) since the carboxylate group bears aformal negative charge and methyl group bears positive charge compared to the lone pair electron at the oxygen atom on the PVP carbonyl group as

shown in Fig7A, B and C. As the PVP–Fe^{3+} interaction is not as strong as CTAB and CMC, this results in slower Fe cluster nucleation when sodium borohydride was introduced. Generally, slow cluster nucleation leads to the formation of larger particles, as there is sufficient time for cluster agglomeration during the process. The second important difference is that the PVP is neutral compared to CTAB and CMC. This results in weaker electrostatic interactions between Fe and PVP. As such it is a predominantly steric hindrance that prevents further nanoparticle growth, which is not as effective as when both steric and electrostatic interactions limit particle size, as is the case with CTAB and CMC stabilizers (Sakulchaicharoen *et al*., 2010).

Conclusion

Dispersed NanozeroValente iron (nZVI) was synthesized in ethanol mediumby borohydride reduction method under atmospheric conditions by using K-M reactor. K-M reactor gives many advantages like that short time of there action, decreasing of Nano iron size at normal conditions. The characterization of dispersed nZVI was performed using TEM, UV-V is and PSD studies and indicated full dispersion of iron nano particles. From the results of TEM, it was observed that iron nano particles with dispersion with different stabilizers but the best stabilizer for more time is CTAB, that increasing surface area of Nano iron for making another experiment specially for core shell applications.

Acknowledgement

The first author is supported by a scholarship from the Mission Department, Ministry of Higher Education, Government of Egypt, which is gratefully acknowledged. Our sincere thanks are extended to Egypt–Japan University of science and technology (E-JUST) for guidance and support.

Also we would like to acknowledge Prof. Kazuhiro Mae (Environmental Process Engineering Lab.) and Dr. Satoshi Watanabe (Surface Control Lab.), Chemical Engineering Department, Graduate School of Engineering, Kyoto University for their valuable advices, guidance and providing the K- M reactor

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