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Green Cost Effective Method for Nano zinc oxide Preparation as Marine Antifouling Additive via Wet Chemical Reduction Method.

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ABSTRACT

Currently nano zinc oxide received great attention in many industrial applications especially in paint industry. Due to the high antimicrobial and antifungal actions of nanosized zinc oxide particles, it could be used as excellent antifouling additive in marine coating polymers. Nanosized of 20nm to 50nm especially 45nm are the optimum particle size of nano zinc oxide which could be used as marine antifouling additives in paint composition. Investigation of optimum operating conditions for the preparation of 45nm nano zinc oxide particles was the target of this study. Wet chemical reduction method via hydroxyethyl cellulose (HEC) as green reducing and stabilizing agent was used. The results show that optimum conditions were zinc ion concentration 1.3g/l, HEC concentration 2.9g/l, at reaction temperature of 80°C for interval time 60min. at stirring rate of 150rpm and pH of 11, to reach maximum percentage obtained of the target size (45nm) 74%.

Key words: nano zinc oxide, marine, antifouling, and chemical reduction.

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INTRODUCTION

Zinc oxide (ZnO) is an important basic material due to its low cost, large band gap, and luminescent properties (Zhong *et al* 1993) It is widely used in many applications, such as catalyst (M.Yoshimoto 1998), gas sensors (Lehman & R. Widmer 1973), filtering materials for ultraviolet light (Ohshima 1993), transparent conductive oxide (Minami 2000) , and in painting industry for coatings formulations against corrosion and micro-organisms, also in prevention of formation of marine biological fouling. Paints containing nano materials such as zinc oxide inhibit the adhesion of microbes and marine fouling organisms. Establishment of nano-structure results in appreciable reduction in interaction between germs and surface. Nano zinc oxide particles help in reduction of germs, virus, and algae by oligodynamic effect of metal oxide component. Nanosized zinc oxide currently used in some sunscreens, as it absorbs and reflects ultraviolet (UV) rays. This may explains its great ability to kill microorganisms such as bacteria, viruses and algae. Incorporating nanoparticles (silver, titanium oxide, zinc oxide, cuprous oxide, etc) in paints could improve their performance, for example by making them lighter and giving them different properties. It may also be possible to reduce solvent content of paints, with resulting environmental benefits. New types of fouling resistant marine paints could be developed and are urgently needed as alternatives to tributyl tin (TBT), now that the ecological impacts of TBT have been recognized. Anti-fouling surface treatment is also valuable in process applications such as heat exchange, where it could lead to energy savings. If they can be produced at sufficiently low cost, fouling-resistant coatings could be used in routine duties such as piping for domestic and industrial water systems. It remains speculation whether very effective anti-fouling coatings could reduce the use of biocides, including chlorine. Two main factors significantly differentiating the properties of nanomaterials than the other forms of materials: huge increment in surface area, and quantum effects, which greatly affecting properties such as reactivity, strength and electrical characteristics. As a particle decreases in size, a greater proportion of atoms are found at the surface compared to those inside. Thus nanoparticles have a much greater surface area per unit mass compared with larger particles. As growth and catalytic chemical reactions occur at surfaces, this means that a given mass of material in nano size will be much more reactive than the same mass of material made up of larger particles. Nano sized zinc oxide powder is one of the most successful marine biological fouling inhibitors and the most suitable size to be used is ranged from 35nm to 50nm. On the other hand to obtain accurate preparation method ensuring highest percentage of the target nano size range (35-50nm) is to be the most difficult obstacle facing researchers in this area. The preparation of different sizes and shapes of ZnO is often studied in previous reports (Hu, *et al* 2001). Various chemical methods adopted for the preparation of metal oxide nanoparticles include the gas-phase methods, sol–gel methods, evaporative decomposition of solution and wet chemical synthesis. (Zhou *et al* 1999,, Jezequel *et al* 1995, Eilers 1995, Milosevic and D. Uskokovic 1993, Takuya and, G.M. 2001, Nishizawa and K. Yuasa 1998, Li *et al* 2000, Fang *et al* 2003, and Liu *et al* 1999). In this work the optimum conditions for preparation of controllable nanosized zinc oxide particles mainly 45nm (to be used as antifouling agent in marine coatings) using hydroxyl ethyl cellulose as reducing agent were investigated. The main controlling parameters to be studied were pH, reaction temperature, stirring time, concentration of reducing agent and metal ion source concentration. Lu sun et al 2008 show that, Zinc oxide is photoactive and generates superoxide and hydroxyl radicals (Reactive Oxygen Species; ROS) when irradiated with UV in the presence of oxygen and water (Lu Sun *et al* 2008). Zinc Oxide has recently achieved special attention regarding potential electronic application due to its unique optical, electrical and chemical properties (Baxter, and E.S .Aydil 2005). The availability of a wide range of nanostructures makes ZnO an ideal material for nanoscale optoelectronics (Huang *et al* 2001) and piezoelectric nanogenerators (Song, *et al* 2006) as well as an efficient material for biotechnology (Wang 2004). Furthermore, ZnO appears to be strongly resisted to microorganisms (Sawai *et al* 1996). There are some reports (Sawai, and T.Yoshikawa, 2004) on the considerable antibacterial activity of CaO, MgO and ZnO, which is attributed to the generation of reactive oxygen species on the surface of these oxides. The advantage of using these inorganic oxides as antimicrobial agents is that they contain environmentally safe mineral elements essential to humans and exhibit strong activity even when administered in small amount. The activity is quantitatively evaluated by studying the growth medium caused by the bacterial metabolism (Sawai, *et al* 2002) Many researchers have attempted to correlate the biological activity of inorganic antibacterial agents with the size of the constituent particles (Brayner *et al* 2006, Stoimenov *et al* 2002). The advantages of inorganic antibacterial materials over organic antibacterial materials are that the former show superior durability, less toxicity, greater selectivity and heat resistance. TiO_2 and ZnO nanostructures have been extensively studied as antimicrobial agents due to their photo catalytic activity under UV light (Fortuny *et al* 1999, Rana *et al* 2006) these antimicrobial substances based on inorganic chemicals have also been found to be effective for therapy. The stunning development and the technological revolution in the field of advanced nanomaterials has led to Strategic applications in many industrial fields such as Autos or airplanes, computers or chips, medicines or cosmetics, chemicals or coatings, construction and energy. All of above mention industrial sectors, and many more, now facing the heat of nanotechnology and going to benefit immensely from its application.

EXPERIMENTAL WORK

Materials

Hydroxyethyl cellulose (HEC), isopropanoal, zinc nitrate, sulfuric acid, and sodium hydroxide (all of high laboratory grade) were used for this study. Reducing agent formula used was also acts as the stabilizer for synthesized nanosized zinc oxide colloids.

Experimental Method

Preparation of the reducing agent formula:

Hydroxyethyl cellulose polymer was heated with 10% isopropanoal solution in slightly alkaline conditions at 40oC till the formation of transparent gel. The obtained gel was added as reducing and stabilizing agent for the zinc oxide nanosized particles.

Preparation of Nanosized zinc oxide Particles

Fixed weight of HEC gel was dissolved in distilled water using heating magnetic stirrer at 40°C. After complete dissolution, the pH of the solution was adjusted to the desired value, followed by raising the temperature of the reaction medium to the desired temperature. Zinc nitrate solution was then added drop wise. The reaction mixture was kept under constant rate of stirring (150rpm) for the desired experiment duration. Once the addition of zinc nitrate, the reaction medium acquires a clear white color converted to dense white indicating the formation of zinc oxide nanoparticles. The propagation of the reaction was controlled by UV–Vis absorption; aliquots from the reaction bulk were withdrawn at given time intervals and evaluated.

Testing and evaluation:

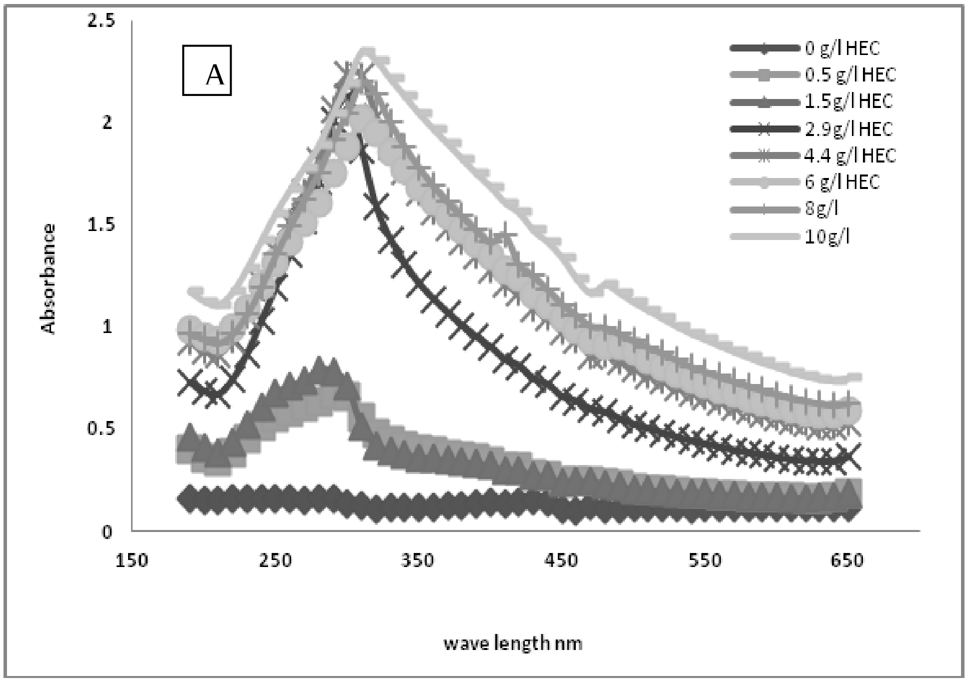
Ultra violet–visible spectra have been proved to be quite sensitive to the formation of nano zinc oxide particles because they exhibit an intense absorption peak due to the surface Plasmon excitation (it describes the collective excitation of conduction electrons in a metal). The UV–Vis spectra of zinc oxide nanoparticles embedded in HEC were recorded by means of a 50 ANALYTIKA JENA Spectrophotometer from 300 to 550 nm. A solution containing zinc nitrate dissolved in de-ionized water was used as a blank.

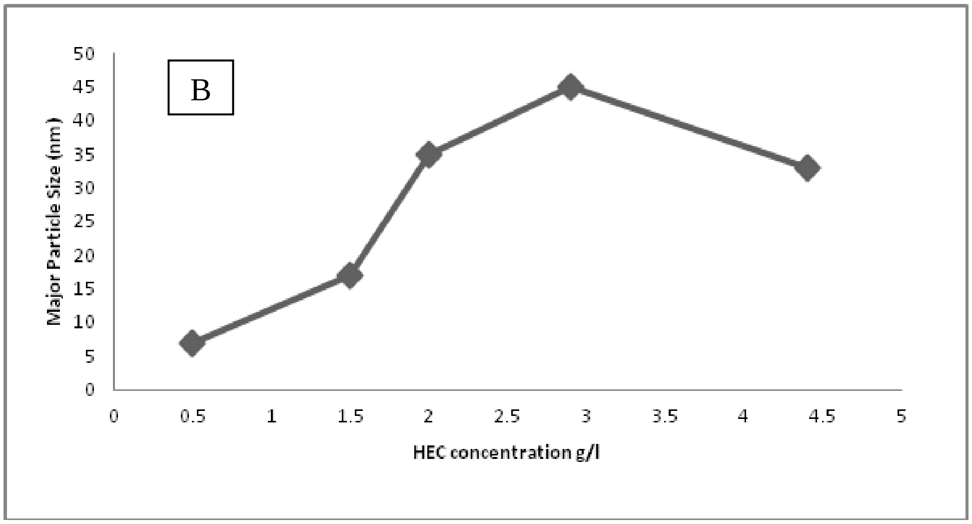
Shape and size of the obtained nanosized zinc oxide particles were characterized by means of a JEOL-JEM-1200 Transmission Electron Microscope (TEM). The TEM sample was prepared by adding a drop of the nano sized oxide solution on a 400 mesh copper grid coated by an amorphous carbon film and lifting the sample for drying in air at room temperature. The average diameter of the zinc oxide nanoparticles was determined from the diameter of 100 nanoparticles found in several chosen areas in enlarged microphotographs. Also the same apparatus used for the examination of the morphology and X-ray diffraction (XRD) test of the obtained particles.

RESULTS AND DISCUSSION

Effect of HEC concentration

Fig. 1A shows the UV–Vis absorption spectra of zinc oxide nano particles prepared using HEC in different concentrations up to 10 g/l, zinc ion concentration of 1.3g/l at initial pH of 9 and temperature of 80°C for 30min and stirring rate of 150rpm. Regardless of the HEC concentration, similar Plasmon bands are formed at wavelength 299nm with the formation of the ideal bell shape which is characteristic for the formation of zinc oxide nano particles. It is clear also that there is a gradual increase in the absorption intensity, by increasing the HEC concentration up to 2.9g/l then no increase in the peak intensity obtained as the HEC concentration increases this could be attributed to the enhancement in the stabilization efficiency of the formed zinc oxide nano particles. Fig. 1B shows the variation of the major obtained zinc oxide nanosized particle due to the variation of the HEC concentration. As HEC concentration increases the particle size increases to reaching 45 nm at HEC concentration 2.9g/l, then the particle size start to decrease with more increment of HEC concentration. The desired particle size 45nm is obtained as major particle size at HEC concentration 2.9g/l, so this value is taken as the optimum HEC concentration. Fig. 1C shows the particle size distribution and its percentage at the optimum selected sample, it is clear that the desired particle size 45nm percentage reached about 31% at the reaction conditions. More control in the reaction conditions have to be carried out to maximize the required particle size percentage. Fig. 1D shows the TEM image of obtained nano zinc oxide with HEC concentration of 0.7g/l, while Fig. 1E shows the TEM image obtained for nano zinc oxide at HEC concentration 2g/l. Fig 1F shows the TEM image of the obtained zinc oxide nano particles using HEC concentration of 2.9g/l which is the selected optimum hydroxyethyl cellulose.





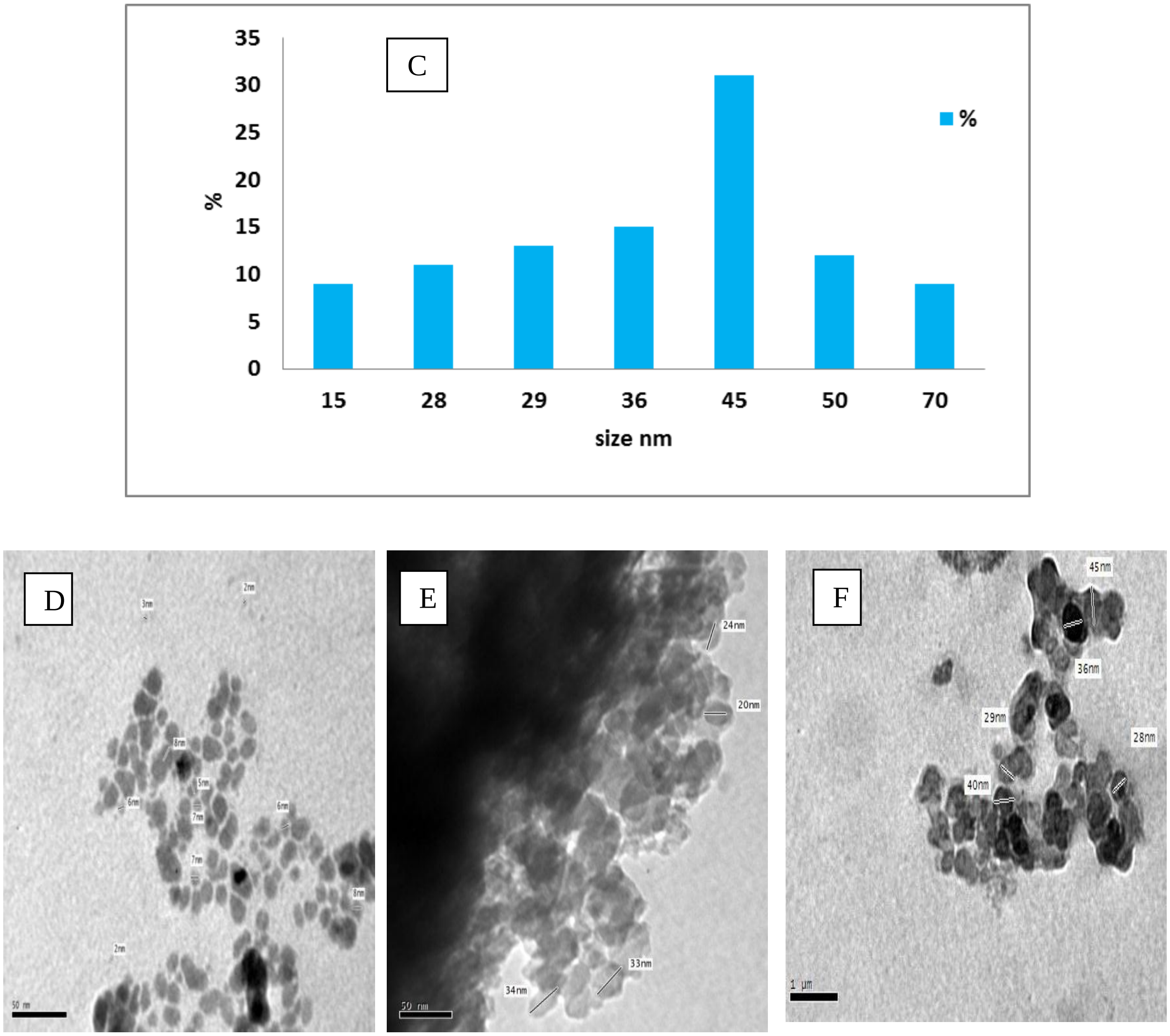
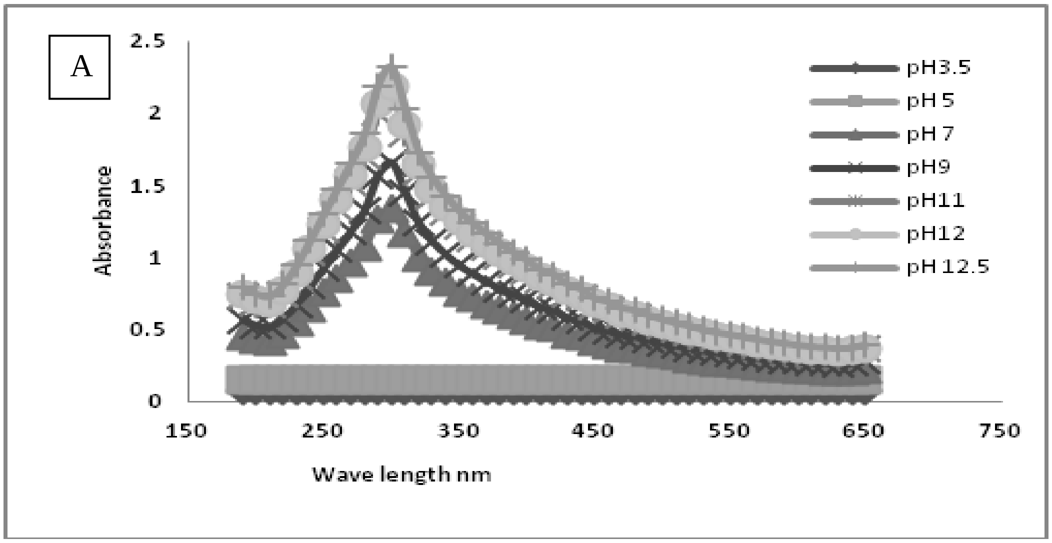
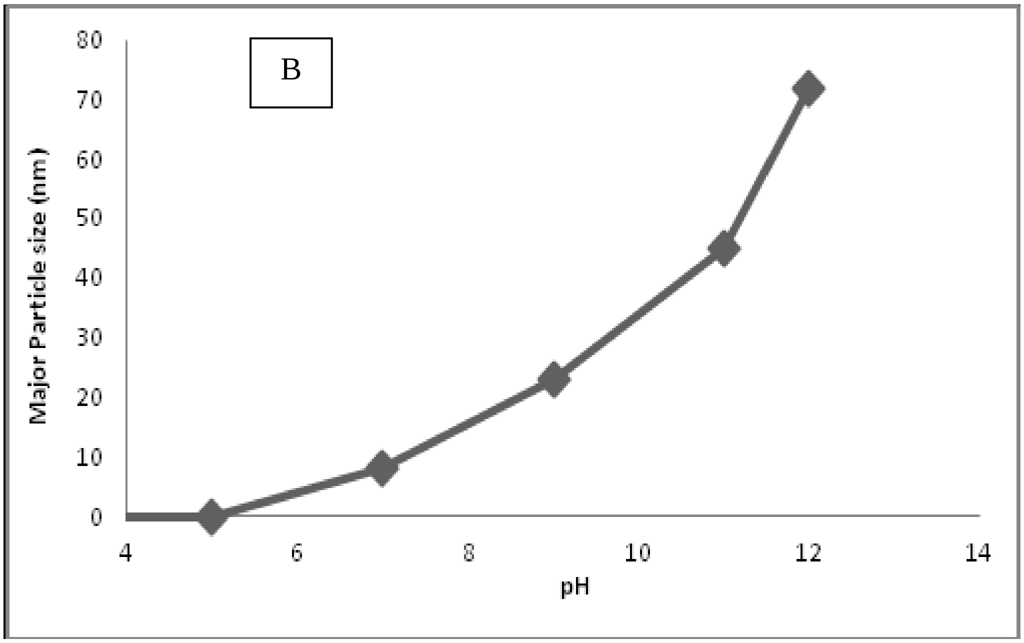


Fig.1 (A) UV–Vis spectroscopy of zinc oxide nano particles prepared at different HEC concentration. Reaction conditions: pH 9, 1.3g/l Zn^{++}; 80^0C. 30min., stirring rate 150rpm, (B) variation of major obtained particle size of nano zinc oxide due to variation of HEC concentration. (C) Histogram for particle size distribution percentage of the sample where the 45nm is the major present particle size and (D, E &F) TEM images of zinc oxide nano particles formed after 30 min at different HEC concentrations.

Effect of pH

Fig. 2A shows the UV–Vis spectra of the zinc oxide colloid obtained using HEC (2.9 g/l) as reducing and stabilizing agent at different pH, at zinc ion concentration 1.3g/l, reaction temperature 800C, reaction duration 30min, and stirring rate of 150rpm.The results show that, increasing the pH of the solution is accompanied by increasing of the intensity of the obtained peak at 299nm; this peak reaches its maximum intensity at pH 12.5 with a pronounced bell shape. This band could be assigned to the Plasmon resonance of zinc oxide nanoparticles. Fig. 2B shows the variation of the obtained major particle size of the nanosized zinc oxide due to variation of the pH value. The results show that as the pH value increases the particle size also increases and the shape of the particles changed from semicircular shape at pH 11 at Fig. 2C to flakes shape at pH 12.5 as shown in Fig. 2D. The reductive properties of HEC are substantially enhanced owing to the oxidative degradation with the formation of low molecular weight reducing chains. The maximum intensity of the Plasmon peak obtained at 299nm at pH 12.5 indicates full reduction of zinc ions and, therefore, reflecting the dual role of HEC as stabilizing and efficient reducing agent in alkaline medium. From the above results pH of 11 was taken as the optimum pH for the target of our study which is the preparation of 45nm zinc oxide nanosized particles as the major present species.





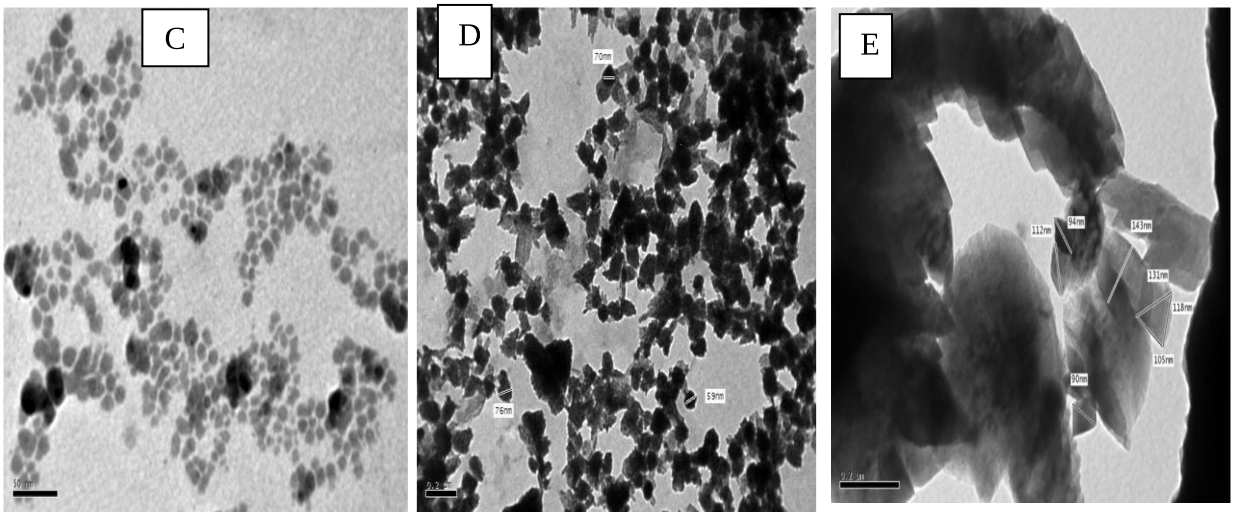
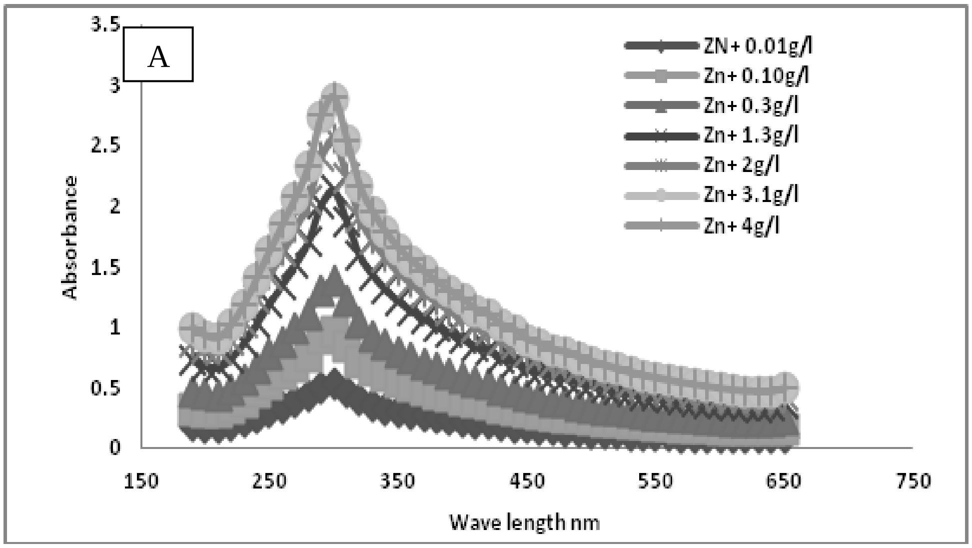


Fig. 2 (A) UV–Vis spectroscopy of zinc oxide nano particles prepared at different pHs. Reaction conditions: 2.9g/l HEC, (1.3g/l) zinc nitrate; temperature 80^{0}C; duration 30 min., and stirring rate 150rpm (B) variation of major obtained particle size of nano zinc oxide due to variation of pH value. (C) TEM image of the sample obtained at pH 11, (D) TEM image obtained at pH 12.5, and (E) is TEM image obtained at pH 14

Effect of zinc ion concentration

Applications of nanosized zinc oxide particles in paint industry acquire large production, so study was undertaken where zinc ion was incorporated at different concentrations in the reaction medium. Fig. 3A shows the UV–Vis spectra of ZnO resulting from incorporating different amounts of zinc ion (0.01–4g/l) and fixing HEC concentration at 2.9g/l for all zinc nitrate concentrations at pH 11, reaction temperature 80^{0}C, reaction duration 30min., and stirring rate 150rpm. Fig. 3A reveals that similar absorption spectra are obtained at wavelength 299nm and that the intensity of the absorption peak increases by increasing zinc nitrate concentration in the reaction medium. Fig. 3B shows that as the concentration of zinc ion source increases the major obtained particle size increases till reaching 45nm at 1.3g/l Zn^{++}, then any increases of the zinc ion concentration leads to decrease of the obtained major particle size. It is found that the ratio of zinc ion concentration to HEC concentration have to be in the order of 0.45 to be assure complete conversion of the ionic zinc to nanosized colloidal zinc oxide with major particle size of 45nm. Hence, preparation of zinc oxide nanoparticles was carried out using higher concentrations of both zinc nitrate and HEC. Fig. 3D shows the TEM micrograph and the particle size distribution histogram when zinc oxide nanoparticles were prepared using zinc ion source concentration to HEC concentration at 0.45 per 50 ml reaction medium. While Figs. 3C and 3E show the TEM micrograph and the particle size distribution histogram when zinc oxide nanoparticles were prepared using zinc ion source concentration to HEC concentration ratio at 0.03 per 50 ml reaction medium. The image show that at this concentration ratio the entire zinc ion converted to 6nm nanosized zinc oxide particles. From all the above results zinc ion source concentration to HEC concentration ratio of 0.45 is taken as the optimum for preparation of major particle size 45nm nanosized zinc particles as our target in paint application.


A
Absorbance
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3
2.5
2
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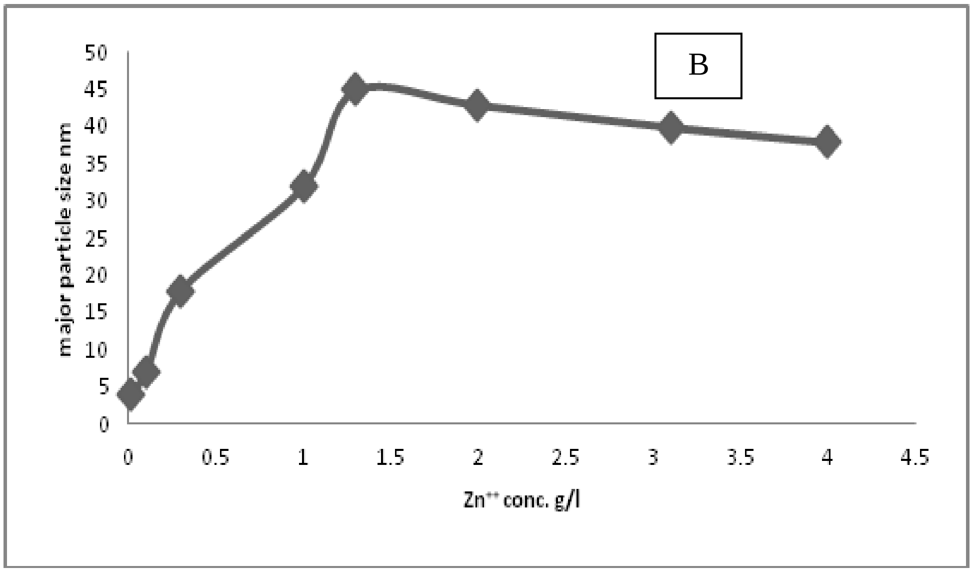
1
0.5
0
150
250
350
450
550
650
750
Wave length nm
ZN+ 0.01g/l
Zn+ 0.10g/l
Zn+ 0.3g/l
Zn+ 1.3g/l
Zn+ 2g/l
Zn+ 3.1g/l
Zn+ 4g/l


B
major particle size nm
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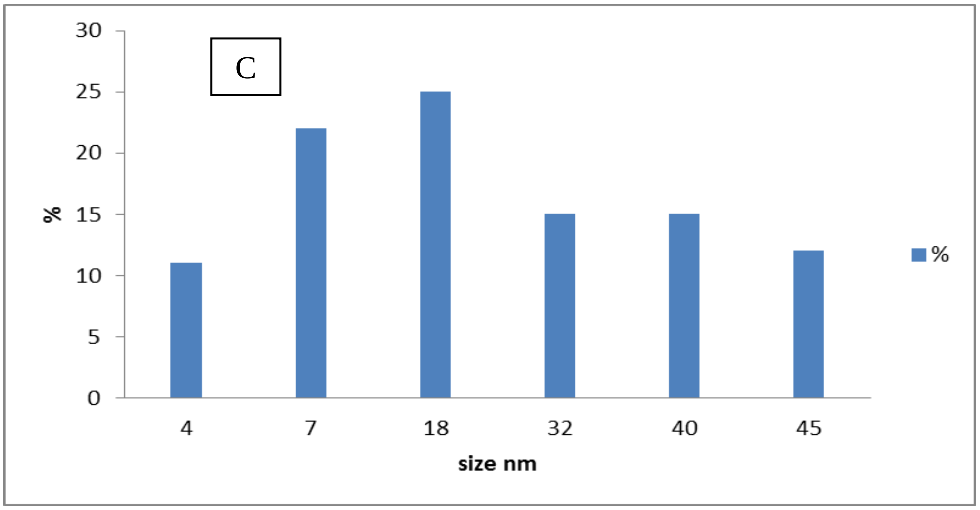
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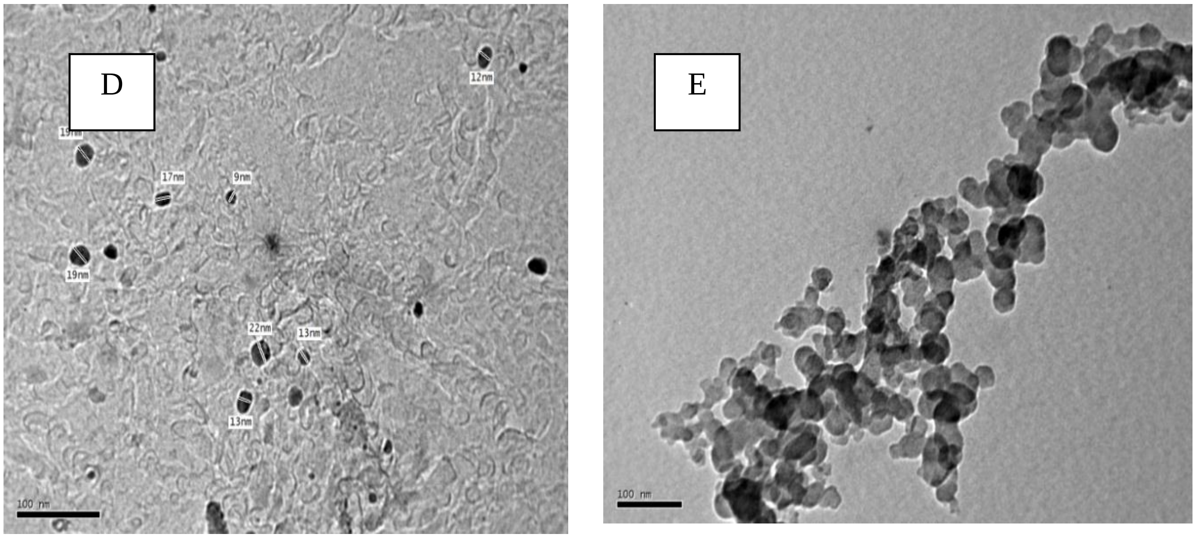
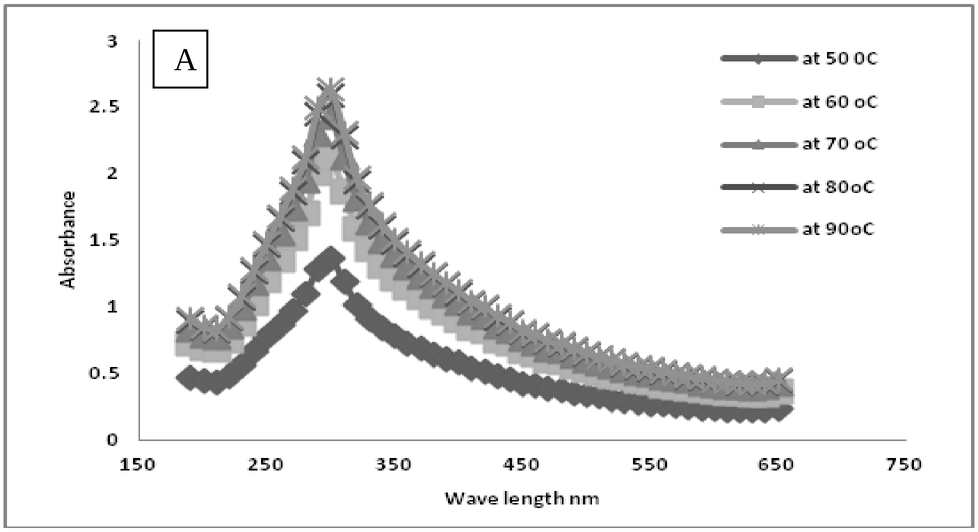


Fig.3 (A) UV–Vis spectroscopy of zinc oxide nanoparticles prepared at different zinc ion concentrations. Reaction conditions: 2.9g/l HEC, (pH 11; temperature 80^{0}C; duration 30 min., and stirring rate 100rpm (B) variation of major obtained particle size of nano zinc oxide due to variation of zinc ion concentration. (C) Particle size distribution histogram and (D) TEM image of the sample obtained at zinc ion concentration of 0,01g/l and HEC concentration of 2.9 g/l, (E) TEM image of the sample obtained at zinc ion concentration of 1.3g/l and HEC concentration of 2.9 g/l

Effect of Reaction Temperature

Fig. 4A shows the UV–Vis spectra of nanosized zinc oxide particles prepared at different temperatures. The data indicate that at 50^{O}C the reduction efficiency is not enough for complete transformation of Zn^{++} into zinc oxide nanoparticles. Increasing the reaction temperature from 50^{0}C to 80^{0}C increases the major particle size from 19nm to 45nm, respectively as clear from Figure 4B also at 80^{O}C the 45nm major particle size present percentage is about 49% which is the maximum as indicated in Fig. 4C. Also there is significant enhancement in the absorption band by rising the temperature up to 80^{O}C. It is also clear from the data that preparation of zinc oxide nanoparticles at 80^{O}C represents the optimum condition, taking in mind the TEM images as fig. 4F and particle size distribution histograms of zinc oxide nanoparticles prepared. Fig. 4D shows the TEM image of nano zinc oxide obtained by HEC at reaction temperature of 50^{O}C, while fig. 4E shows the TEM image of nano zinc oxide obtained by HEC at reaction temperature of 60^{O}C.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Absorbance
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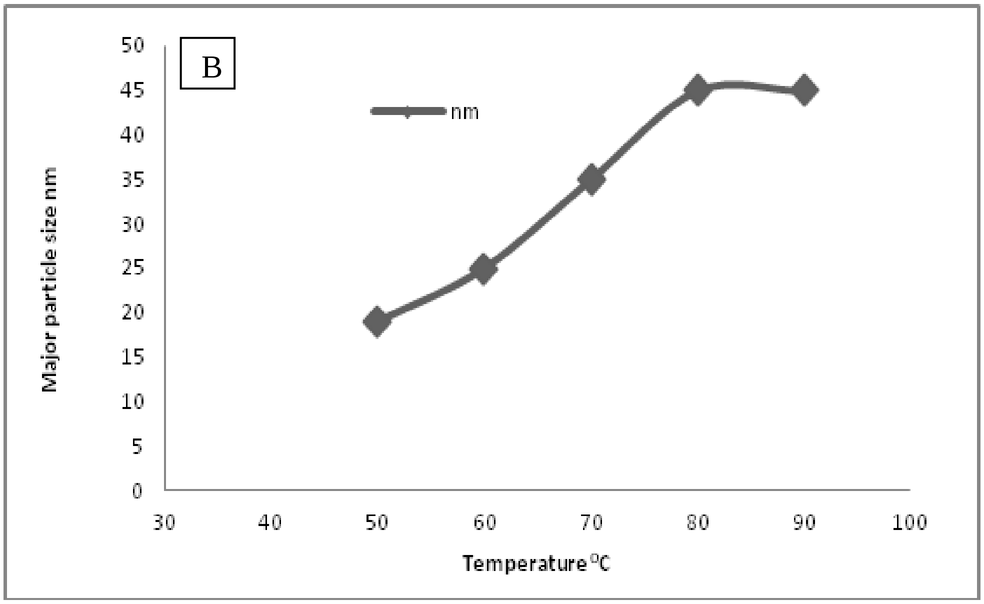
Wave length nm
at 50 0C
at 60 oC
at 70 oC
at 80oC
at 90oC


B
Major particle size nm
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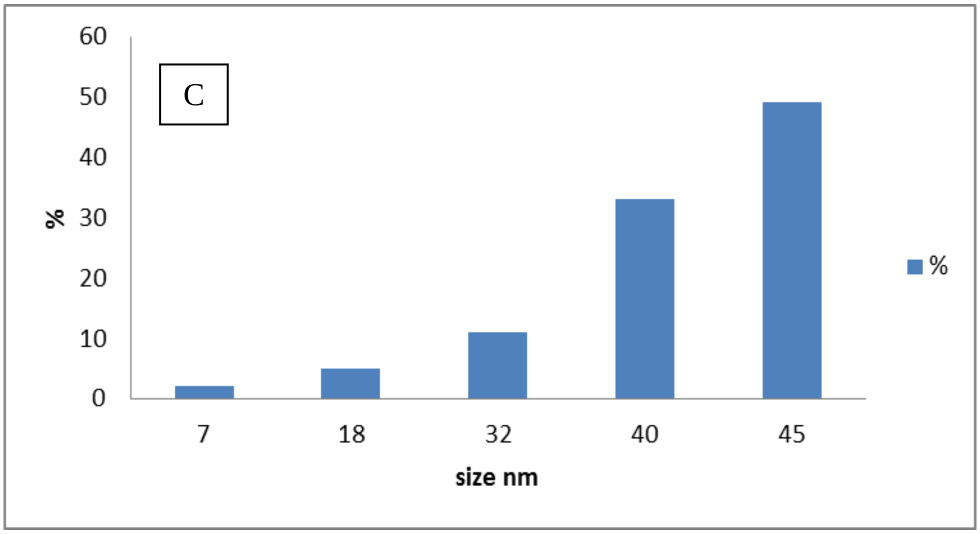
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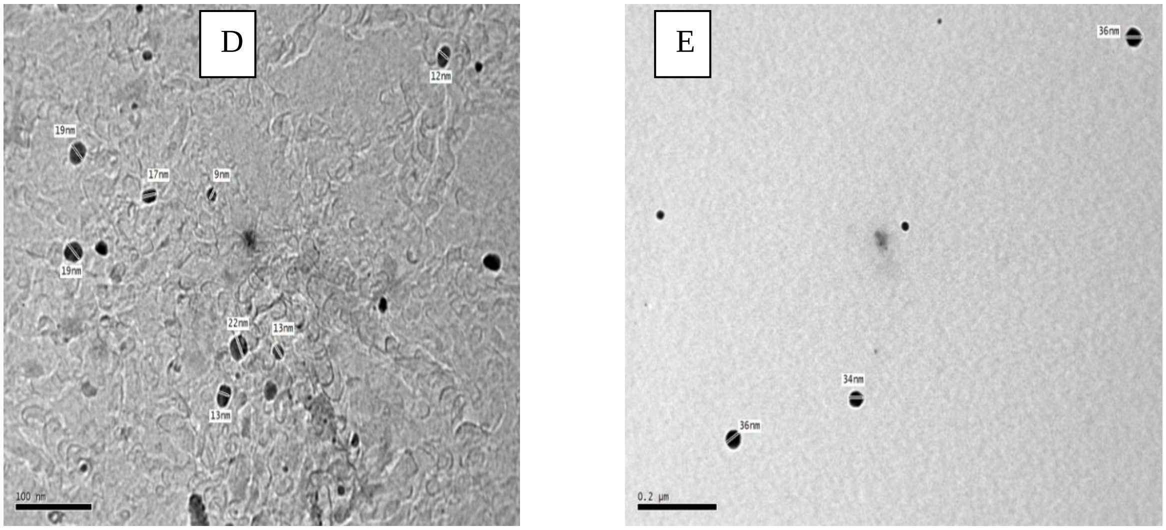
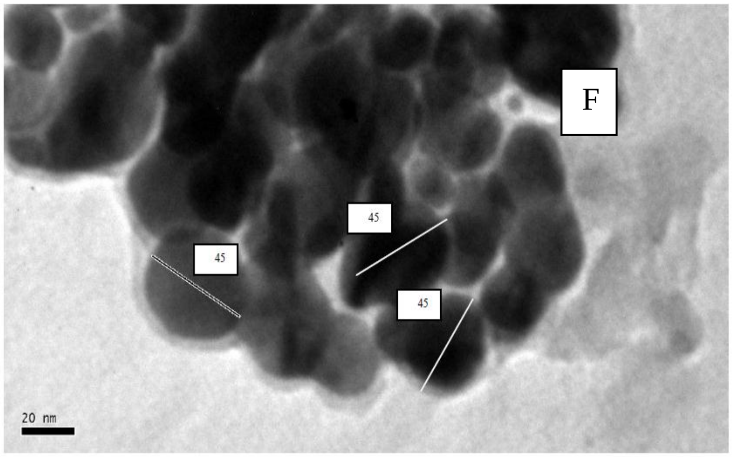


50°C 60°C



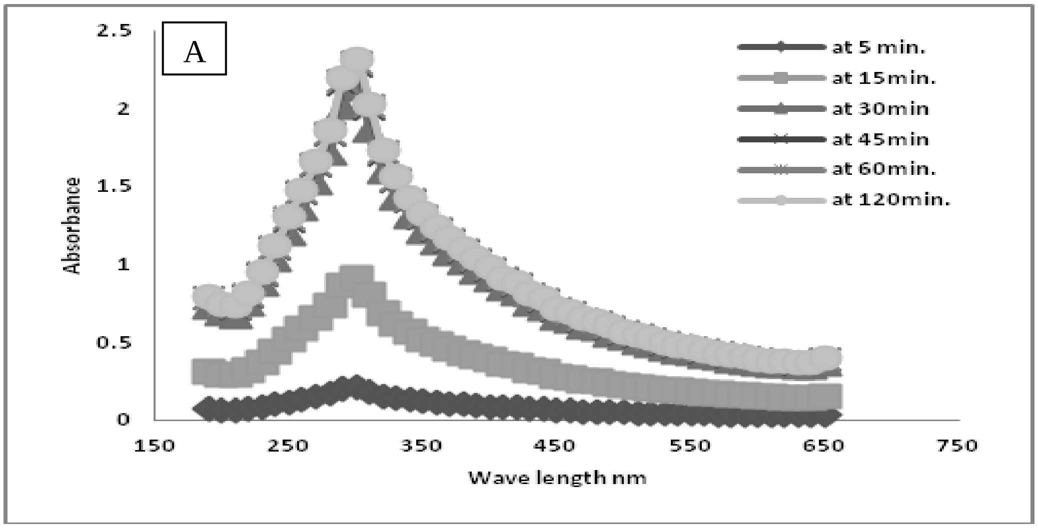
80°C

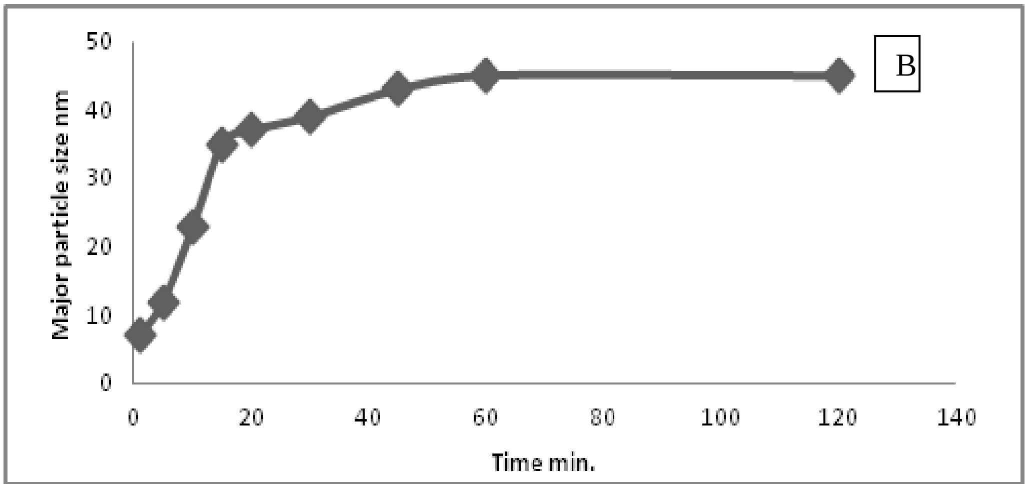
Fig.4 (A) UV–Vis spectroscopy of zinc oxide nanoparticles prepared at different reaction temperatures. Reaction conditions: zinc ion concentration 1.3g/l, 2.9g/l HEC, pH 11; duration 30 min., and stirring rate 150rpm (B) variation of major obtained particle size of nano zinc oxide due to variation of reaction temperature. (C) Particle size distribution histogram and (D) TEM image of the sample obtained and (E) TEM image of the sample obtained at reaction temperature of 60°C. (F) TEM image of the sample obtained at reaction temperature of 80°C.

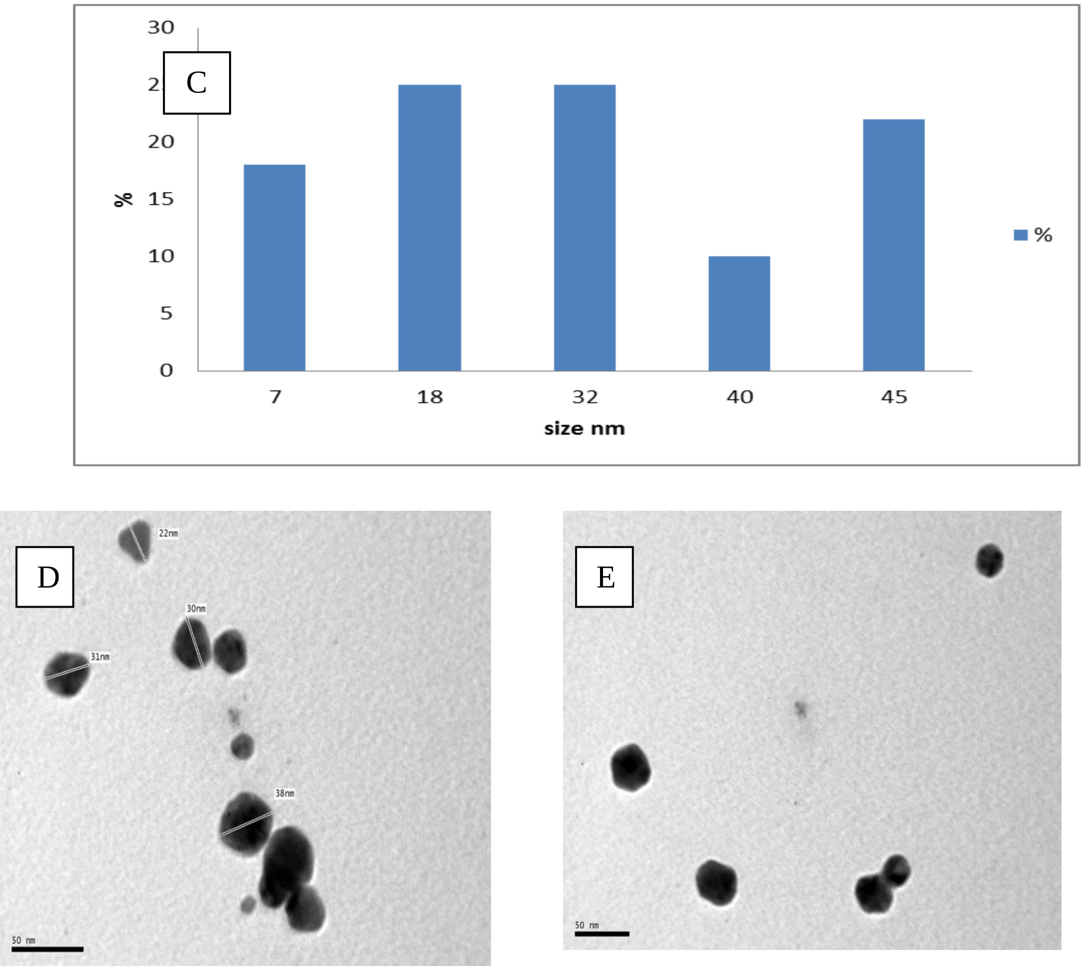
Effect of reaction Time

Fig. 5A shows the UV–Vis absorption spectra of zinc oxide nanoparticles colloidal solutions prepared at different durations. The operating conditions were HEC 2.9g/l, zinc nitrate concentration 1.3g/l, pH 11, reaction temperature 80°C, and stirring rate of 150rpm. The data revealed several important findings which can be presented as follows: (i) at the early stage reaction duration (after 5 min) the Plasmon band is broaden and simple test for zinc ion using NaCl solution indicates low conversion of zinc ions to zinc oxide nanoparticles at this duration, (ii) prolonging the reaction duration up to 45 min leads to outstanding enhancement in the

Plasmon intensity indicating that large amounts of zinc ions are reduced and used for cluster formation, (iii) further increase in the reaction duration up to 90 min is accompanied by marginal decrement in the absorption intensity which could be attributed to some aggregation of the formed zinc nanoparticles, (iv) increasing the reaction duration up to 120 min leads to significant decrease in the absorption intensity. Fig. 5B shows the obtained major particle size present due to the variation of the reaction duration. The results show that as the reaction duration increases the obtained major particle size present increases to reach its maximum 45nm at duration time 45min. then any increment in reaction duration does not affect the obtained particle size. Fig. 5C shows he particle size distribution histograms of zinc oxide nanoparticles formed after 15min while Fig. 5D shows the TEM images and the particle size distribution histograms of zinc oxide nanoparticles formed after 45min. TEM image shows small size spherical particles 7nm after 5min. while it reaches 45nm after 60min. also The corresponding size distribution histogram clearly illustrates that the target size 45nm reaches its maximum percentage at reaction duration 60min. From the above 60min. reaction duration was taken as the optimum.





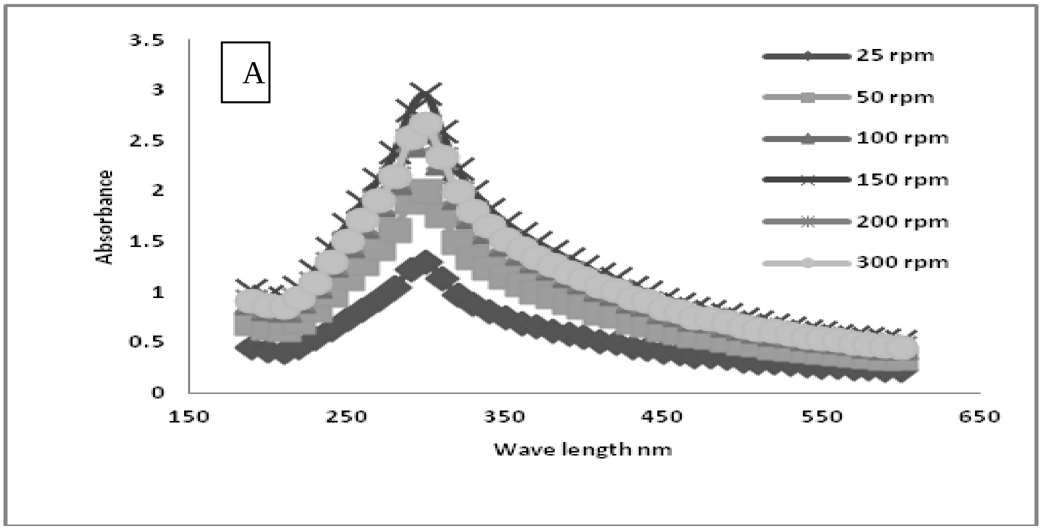


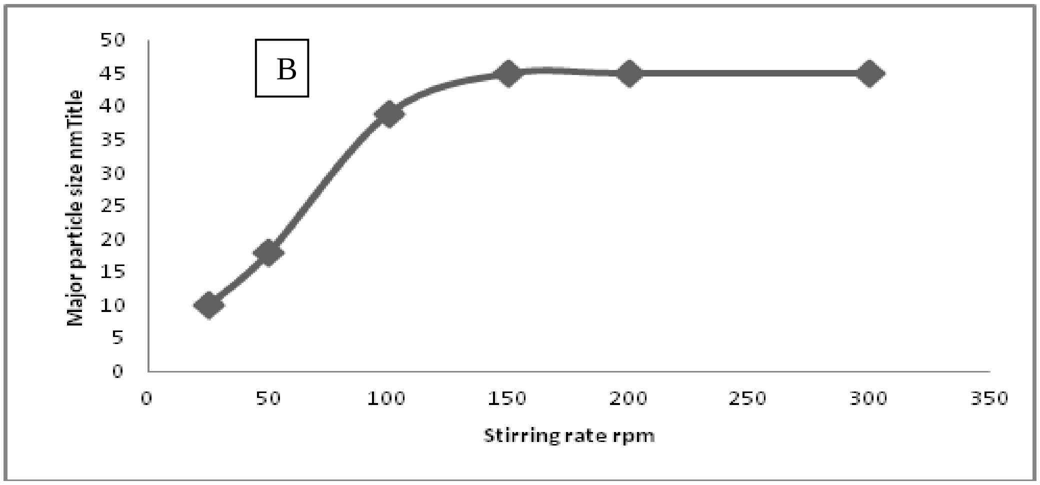
15min **60min.**

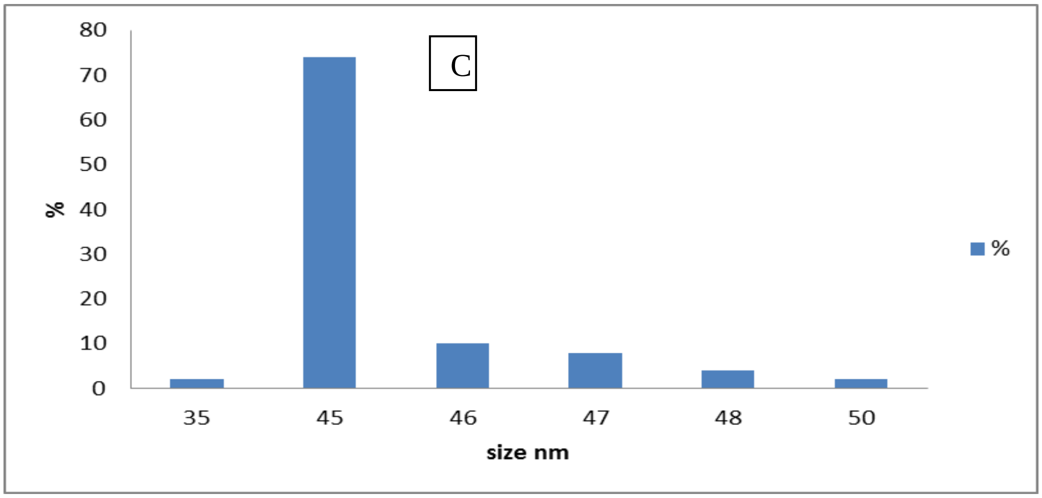
Fig. 5 (A) UV–Vis spectroscopy of zinc oxide nanoparticles prepared at different reaction time. Reaction conditions: zinc ion concentration 1.3g/l, 2.9g/l HEC, pH 11; 80^{0}C., and stirring rate 150rpm (B) variation of major obtained particle size of nano zinc oxide due to variation of reaction duration. (C) Particle size distribution histogram and (D)TEM image of the sample obtained at 15min.and (E) TEM image of the sample obtained after 60 min..

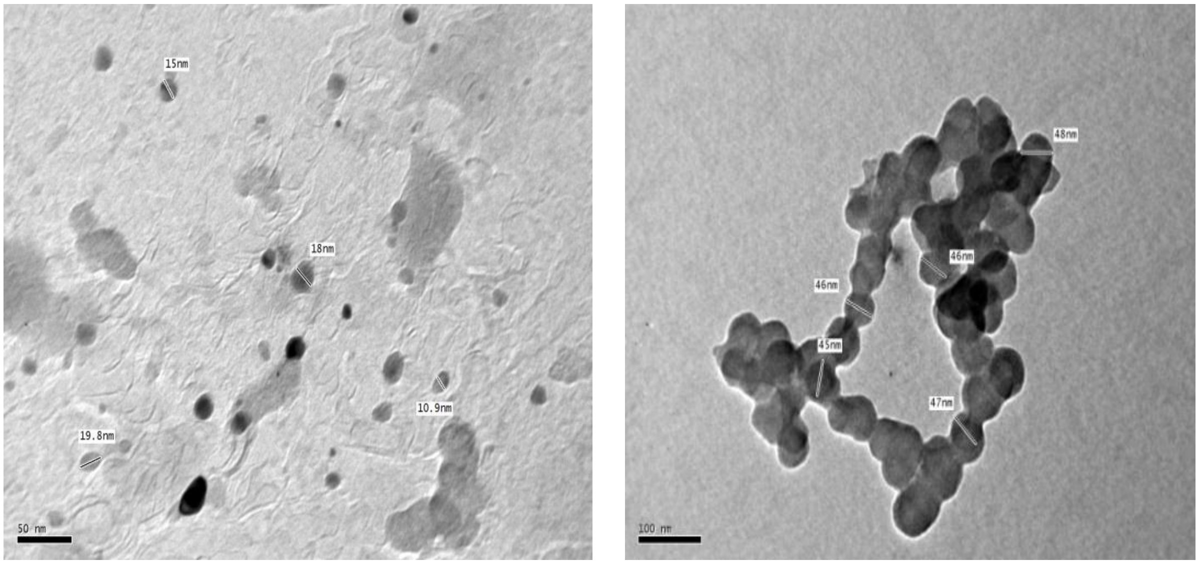
EFFECT of Stirring Rate

Fig. 6A shows the UV–Vis spectra of nanosized zinc oxide particles prepared at different stirring rate. The data indicate that at 50rpm the reduction efficiency is not enough for complete transformation of Zn^{++} into zinc oxide nanoparticles. Increasing the rate of stirring to 150 rpm leads to the increasing of the major particle size present to 45nm and its percentage was 74% as indicated in fig.6B and fig. 6C. Also there is significant enhancement in the absorption band by raising the rate of stirring up to 150rpm. It is also clear from the data that preparation of zinc oxide nanoparticles at 150rpm represents the optimum condition, taking in mind the TEM images and particle size distribution histograms of zinc oxide nanoparticles prepared. From the above its clear that the optimum conditions to get the highest percentage of the desired particle size of nanosized zinc oxide (45nm) which is suitable for marine antifouling paint are: pH of 11, zinc ion source concentration 1.3g/l, HEC concentration 2.9g/l, reaction temperature 80^{O}C, at reaction duration of 60min. with rate of stirring of 150rpm. At these conditions the target nano size of zinc oxide (45nm) percentage reached up to 74%.









At 50rpm at 150rpm

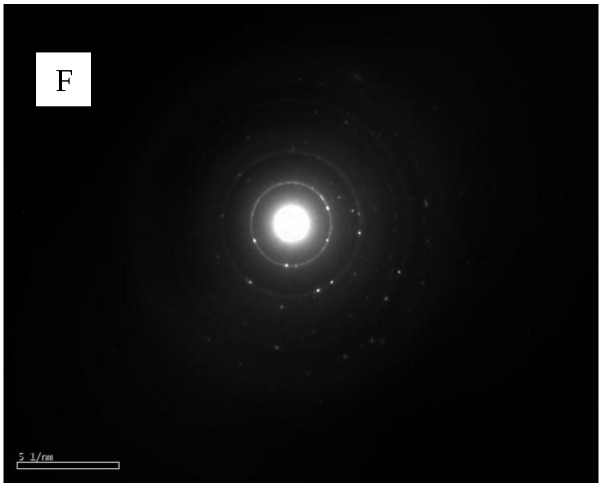


Fig. 6 (a) UV–Vis spectroscopy of zinc oxide nanoparticles prepared at different stirring rates. Reaction conditions: zinc ion concentration 1.3g/l, 2.9g/l HEC, pH 11; 80^{0}C., and duration time 60min. (b) variation of major obtained particle size of nano zinc oxide due to variation of stirring rate. (C) Particle size distribution histogram and (D) TEM image of the sample obtained at reaction temperature of 80^{0}C, zinc ion concentration of 1.3g/l, HEC concentration of 2.9 g/l, at pH 11, reaction duration of 60min., and stirring rate of 150rpm. (E) TEM image of the sample obtained at reaction temperature of 80^{0}C, zinc ion concentration of 1.3g/l, HEC concentration of 2.9 g/l, at pH 11, reaction duration of 60min., and stirring rate of 150rpm. And (F) selected area electronic diffraction pattern (SAED) of nano zinc oxide prepared at the optimum conditions.

CONCLUSION

Nanosized zinc oxide particles of 45nm was prepared in this study as the optimum particle size to use as marine antifouling additive in marine paint composition due to its high antimicrobial and antifungal actions. Wet chemical reduction method was used for the preparation and green hydroxyl ethyl cellulose (HEC) was used as reducing and stabilizing agent. 74% of the desired particle size 45nm was obtained at the optimum operating conditions which are: zinc ion concentration of 1.3g/l, HEC concentration of 2.9 g/l with zinc oxide ion to HEC concentration ratio of 0.45 and reaction temperature of 80^{O}C for duration of 60min. with rate of stirring of 150rpm at pH of 11.

REFERENCES

[1] Baxter JB, and ES Aydil. Appl Phys Lett 2005;86:53114.
[2] Brayner R, R Ferrari-lliou, N Brivois, S Djediat, MF Benedetti, and F Fievet. Nano Lett 2006;6: 866.
[3] Eilers H. BM Tissue, Mater Lett 1995;24:261.
[4] Fang XS, CH Ye, XS Peng, YH Wang, YC Wu, LD Zhang. J Mater Chem 2003;13:3040.
[5] Fortuny A, C Bengoa, J Font, and A Fabregat. J Hazard Mater 1999;64:181.
[6] Hu JQ, XL Ma, ZY Xie, NB Wong, CS Lee, ST Lee. Chem Phys Lett 2001;344: 97.
[7] Huang MH, SMao, H Feick, HQ. Yan, Y Wu, H Kind, E. Weber, R Russo, and P Yang. 2001, In Sers. Science 292.
[8] Jezequel D, J Guenot, N Jouini. J Mater Res 1995;10:77.
[9] Lehman H.W., R. Widmer. J Appl Phys 1973;44:3868.
[10] Li Y GW, Meng LD, Zhang, F Phillipp. Appl Phys Lett 2000;76:2011.
[11] Liu X., J. Ding, J. Wang. J Mater Res 1999;14:3355.
[12] Lu Sun, A John, G Peter, W Xungai, Ken King. Int J Technol 2008;7: 224-235,
[13] Milosevic O, D Uskokovic. Mate. Sci Eng 1993;168:249.
[14] Minami T. MRS Bull 2000; 25 (8):38.
[15] Nishizawa H, K Yuasa. J Mater Sci Lett 1998;17:985.
[16] Ohshima K, K Tsuto, K Okuyama, N Tohge. J Am Ceram Soc 1993;76:65.
[17] Rana S, J Rawat, MM Sorensson, and RDK Misra. Biomater 2006;2:421.
[18] Sawai J, and T Yoshikawa. J Appl Microbiol 2004;96:803.
[19] Sawai J, H Igarashi, A Hashimoto, T Kokugan C and M Shimizu. J Chem Eng Japan 1996;29:556.
[20] Sawai J, R Doi, Y Maekawa, T Yoshikawa, and H Kojima. J Ind Microbiol Biotech 2002;29:296.
[21] Song J, J Zhou, and ZL Wang. Nano Lett 2006,;6:1656.
[22] Stoimenov PK, RL Klinger, GL Marchin, and KJ Klabunde. Langmuir 2002;18:6679.
[23] Takuya T, GM Paul. Scripta Mate 2001;44:1731.
[24] Wang ZL. Annu Rev Phys Chem 2004:55(159): 1656-1662.
[25] Yoshimoto M, S Takagi, Y Umemura, M Hada, H Nakastuji. J Catal 1998;173:53.
[26] Zhong J, AH Kitai, P Mascher, W Puff. J Electrochem Soc 1993;140:3644.
[27] Zhou ZW, H Deng, J Yi, SK Liu S. Mater Res Bull 1999;34:1563.