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Synthesis of Nano-sized Zinc Oxide and Its Application for Cellulosic Textiles

M.A. Ramadan[1], S.H. Nassar[1], A.S. Montaser*[1], E.M. El-Khatib[1]and M.S.Abdel-Aziz[2]
[1]Textile Research Division and [2]Microbial Chemistry Department, NRC, Egypt.

IN THIS article zinc oxide (ZnO) nano-particles are synthesized through the alkali precipitation method using zinc acetate as a precursor and sodium hydroxide as basic source. The characterization of nanosized zinc oxide particles and their application in the pretreatment processes of cotton textiles have been studied for the resistance against bacteria and fungus, color strength enhancement and fastness properties improvement in addition to studying the effect of zinc oxide nano-particles incorporation into the printing paste on fixation method of the prints. The nanoparticles composition as well as their shape, size and crystallinity has been studied by transmission electron microscopy (TEM), X-Ray powder Diffraction (XRD). The synthesized ZnO nanoparticles have particle size lies between 200-300 nm for the calcinated and higher than 400 for the dried one. The synthesized ZnO nano-particle shows antibacterial activity towards microorganisms (bacteria and fungi) and affects positively color fastness of printed fabrics, especially those treated with thermo-fixation process after printing. The results showed that the performances of zinc oxide as finishing agent can significantly improve printed cotton fabrics properties.

Keywords: Zinc oxide nanoparticles, Antibacterial, Steaming, Thermo-fixation

Adding new materials such as nano-metallic particles in the wet processing [(1)] as, printing process is one of these methods. Depending on used dye, there are two major categories of the printing, reactive printing and pigment printing. The reactive printing has the priority for color depth and fastne**ss** properties. Nano-metallic particles have several uses in textile industry[(2-5)] Zinc Oxide nanoparticles have several properties like high thermal conductivity, high refractive index, antibacterial, binding energy[(6)], catalytic activity[(7)] and UV- protection[(8)]. It is widely used in many materials and products. The products include medicine[(9)], cosmetics, rubber, solar cells, foods, pigments [(10)] and textiles finishing [(11)].

There are several methods for synthesis of these ZnO nanoparticles powders such as alkali precipitation, thermal decomposition, hydrothermal synthesis, solgel methods[(12)], microemulsions,spray pyrolysis, template-free method and other routes.

* Corresponding author email: abohabbiba2012@gmail.com

This study addresses the synthesis and characterization of ZnO nanoparticles through the alkali precipitation method using sodium hydroxide as the alkaline source. ZnO nanoparticles were then applied on to printing paste to prepare cotton prints in presence of reactive dye, in addition to its effect on the fixation way of printed samples .The fastness properties and color strength of printed cotton fabrics were evaluated through standardize was procedures.

Experimental

Material and methods

Materials

Zinc acetate dehydrate and sodium hydroxide were obtained from Merck Chemical Company (Darmstadt, Germany), cotton fabrics was supplied by Misr/Helwan for Spinning andWeaving Company, Cairo. Levafix Royal Blue E dye was kindly supplied by Dystar, Germany. All chemicals were used without further purification. Deionized water was used for the preparation of all solution as well as other respective dilutions.

Methods

Preparation of Zinc oxide nanoparticles: The zinc oxide nanoparticles were prepared using precipitation method making use of the zinc acetate and sodium hydroxide. 4N zinc acetate was dissolved at 100 ml water followed by dropwise addition of 4N sodium hydroxide until white precipitate settled from the solution. The mixture heated at 60 ºC for 30 min followed by filtration. The obtained white precipitate dried at 100ºC to form the precursors for the zinc oxide nanoparticles and portions of the zinc oxide nanoparticles were taken and thermally treated at 400ºC for 3 hr. [13].

Characterizations of Zinc oxide nanoparticles: Zinc oxide in solution dropped out of the suspension and was deposited onto carbon film that coated copper grids for characterization by transmission electron microscopy (TEM) which used to characterize the shape and morphology of the obtained nanoparticles. Particle sizes of the sample were characterized by particle size analyzer technique for measuring the size distribution by number. Phase identification of the samples was characterized by X-Ray powder diffractometry (XRD, PW 3040/60 Philips X'Pert, Holland) with Cu (K) radiation (=0.15416 nm) operating at 40 kv and 30 mA with 2 ranging from 10- 90°C for Chemical and Green method [14-16] .

Printing

Printing paste preparation

The printing pastes were prepared according to the following recipe

Dye----------30 g
Urea----------100 g
Resist salt----------10 g
Sodium carbonate----------25 g
ZnO nanoparticles ----------L g = (converted to ppm)
Water ----------y g

Total ----------1000 g
Sodium alginate 4% was used as thickening agent [17].
NB: .0.8 mg of Zinc Oxide dispersed in one liter of Ethylene glycol (EG/Water) (65/35) to produce 1 ppm.

Printing procedure

Printing was carried out by the conventional screen printing technique. Samples printed with the prepared printing pastes containing reactive dye were first dried and then fixated by two ways: a) Steam-fixation: printed samples fixated by steaming at 120-123°C for 10 min. and b) Thermo-fixation: printed samples thermo fixated at 130°C for 3.5 min. The fixation of dye on the fabric carried out at atmospheric pressure[17].

Washing

Washing process of the prints was carried out through four stages: 1)rinsing thoroughly with cold water, 2) washing with hot water , 3) soaping using 2g/l non-ionic detergent namely Espycon 1030at 90-95 °C for 15 min. and 4) washing with hot water. The samples were dried and assessed for color strength and overall fastness properties.

Color strength (K/S) and fastness

Color strength expressed as(K/S), and the fastness properties, washing, perspiration and rubbing, were assessed according to standard methods [18].

Antibacterial activity

Zinc oxide nanoparticles were tested on *Pseudomonas arauginosa* [ATCC 27853] and *Staphylococcus aureus* [ATCC 6538-P] by zone of inhibition experiment in addition to *Asperagillus niger* [NRRL A-326] as a type of fungi which kindly supplied from Microbiological Department , NRC, Egypt . Nutrient agar was poured onto the Petri dishes and allowed to solidify. Bacteria and fungi were spread on three different plates uniformly. Zinc oxide nanoparticles were gently placed over the solidified agar gel. Plates were incubated at 37°C for 24 hr to check the zone of inhibition[19,20].

Results and Discussions

X-ray diffraction spectrometry

Zinc acetate reacts with sodium hydroxide forming weight precipitate of zinc hydroxide and sodium acetate, the obtained precipitate was washed with water to remove sodium acetate. The obtained hydroxide drying at 100°C forming metal alkoxide followed by calcinations at 400°C for 3 hr cleavage the alkoxide chains forming metal oxide nanoparticles. We can describe the zinc oxide formation with the reaction below[13].

$$Zn(CH_3CHOO)_2{:}6H_2O+NaOH \rightarrow Zn(OH)_2+CH_3COONa+6H_2O \ldots\ldots Eq_1$$

$$n\ Zn(OH)_2 \rightarrow (Zinc\ oxide)_n+nH_2O \ldots\ldots Eq2$$

$$(Zinc\ oxide)\ n \rightarrow n Zinc\ oxide \ldots\ldots Eq3$$

Figure 1 (a, b) shows the XRD data of the dried zinc oxide and zinc oxide nanoparticles calcined after the drying process at 400 °C. All of the XRD plots of the composites show peaks from the pure hexagonal structure of zinc oxide. Three reflections (100), (002) and (101) have been observed, which are similar to the observed reflections in zinc oxide bulk. The diffraction peaks obtained at 31.84°, 34.52°, 36.33°, 47.63°, 56.71°, 62.96°, 68.13°, and 69.18° are strong and narrow indicating that the nano-crystalline zinc oxide NPs has good crystallinity. The highest intensity at Fig. 1b related to zinc oxide nanoparticles express the sample particles size reflecting the nano-range size which appears after by particle size analyzer. Also, characteristic peaks of the zinc oxide phase increase in intensity at 400^{o}C with the calcination temperature. The calcined sample may be more purified at this temperature because of losing traces of CH_3COONa after washing, which decomposed gradually with increasing the temperature. The pure phase of zinc oxide was formed at 400°C [13].

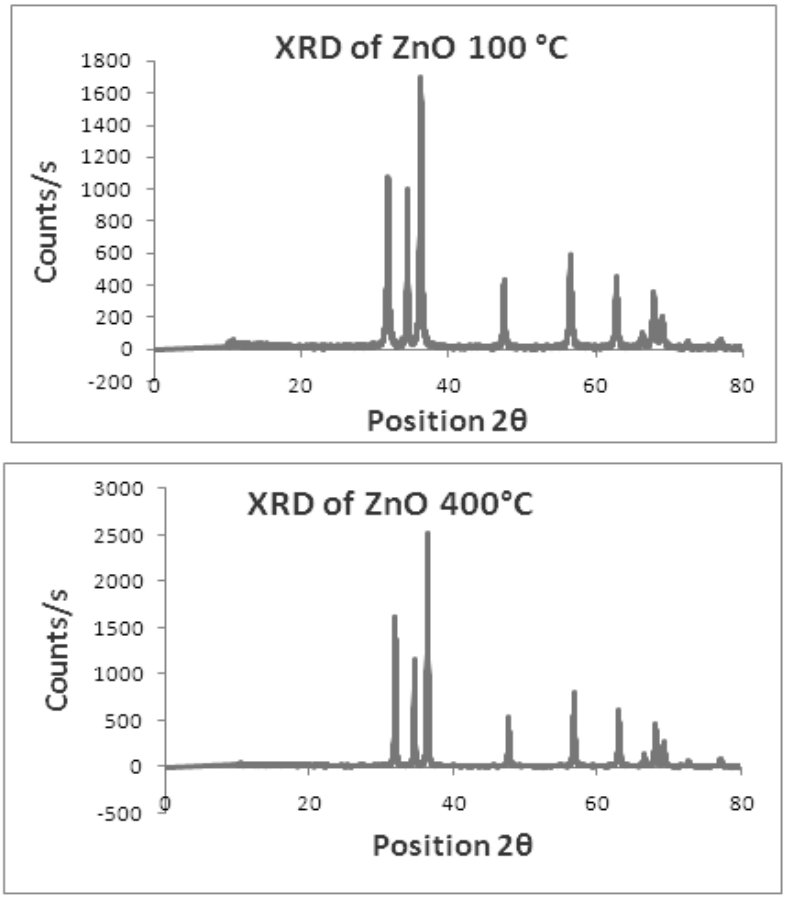

Fig. 1. XRD analysis of (a) ZnO nanoparticles dried at 100 °C, (b) ZnO nanoparticles calcinated at 400°C.

Transmittance electron microscopy

TEM photograph of nanocrystalline zinc oxide nanoparticles at two different temperatures are shown in Fig.2. Sample (Fig. 2a) prepared the precursors of zinc oxide powder at 100°C. The produced powder was amorphous zincite with a nearly spherical structure. The calcinated zinc oxide (Fig. 2b) nanoparticle at 400°C shows homogenous hexagonal structure. It is expected that the temperature of calcinations assist purification and degradation of metal alkoxide bonds forming homogenous and crystalline zinc oxide nanoparticles, it's also expected that water residues completely removed up 100°C affect crystallinity of the produced zinc oxide nanoparticles, it means at 400°C completely removing of water molecules. The results of TEM are consistent with the observation from XRD [13].

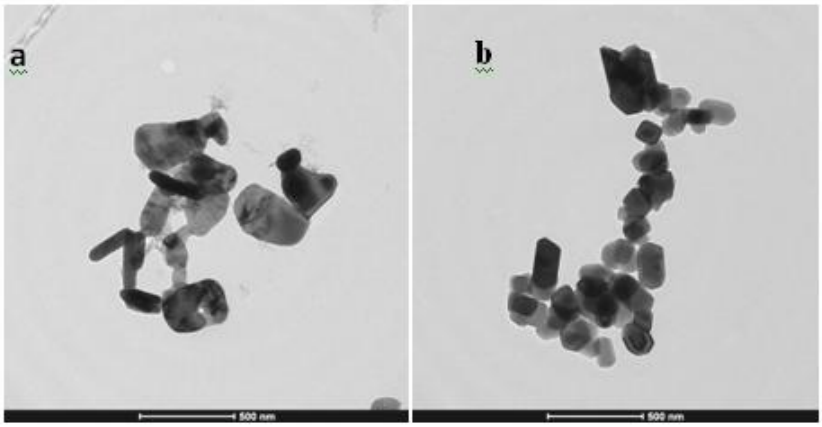

Fig. 2. TEM images of (a) ZnO nanoparticles dried at 100°C, (b) ZnO nanoparticles calcinated at 400°C.

Particle size analyzer

Figure 3 showed increase in the particle size crystal for zinc oxide nanoparticles dried at100ºC over the calcined zinc oxide nanoparticles at 400ºC. The particle size analyzer Fig. 3a shows the widely distributed size for zinc oxide nanoparticles dried at 100 °C are lying between 700-900 nm. On the other hand, Fig. 3b shows boarded distributed size for calcined zinc oxide nanoparticles at 400ºC which decreases to 250 nm. The two prepared forms of zinc oxide nanoparticles lie in submicron. The depression at size with high temperature attributed to temperature effect at removing traces of zinc oxide nanoparticles reaction and completely removing of moisture from internal network of the produced zinc oxide nanoparticles crystal ([13] .

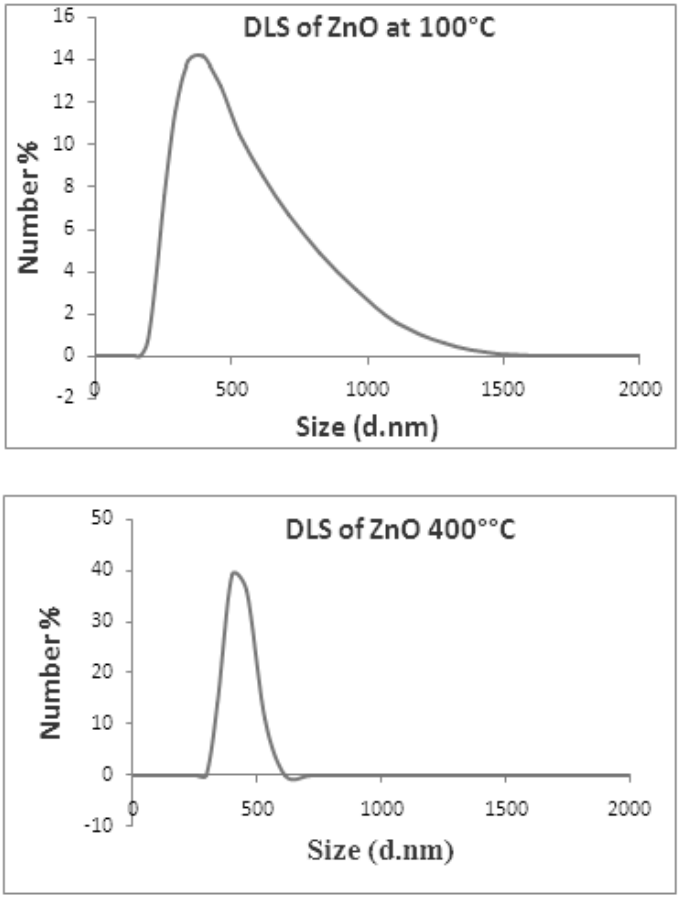

Fig. 3. Particle size analyzer of (a) ZnO nanoparticles dried at 100°C, (b) ZnO nanoparticles calcinated at 400°C.

Antibacterial activity of zinc oxide nanoparticles

In Fig. 4 zinc oxide nanoparticles exhibited remarkable antibacterial activity and demonstrated a lethal effect against all types of microorganisms, disc zone method shows inhibition zone of zinc oxide nanoparticles 12 -15 mm toward microorganisms even at low concentrations. As known a plausible mechanism of zinc oxide inactivation of bacteria involves the direct interaction between zinc oxide nanoparticles and cell surfaces, which affects the permeability of membranes where nanoparticles enter and induce oxidative stress in bacterial cells, subsequently resulting in the inhibition of cell growth and eventually in cell death [21] .

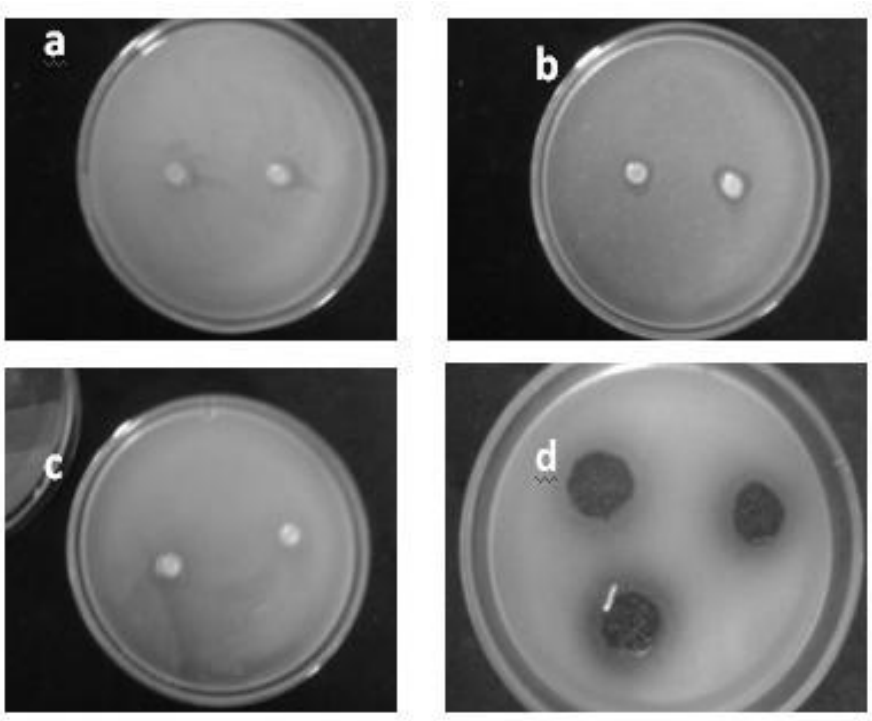

Fig. 4. antibacterial activity of zinc oxide nanoparticles against a) *Staphylococcus aureus*, b) *Pseudomonas arauginosa*, c) *Aspergillus – niger* and d) Printed sample against *Pseudomonas arauginosa*.

Effect of zinc oxide nanoparticles concentration on overall fastness properties of printed fabrics

Four different concentrations of zinc oxide nanoparticles 200 -500 ppm /kg printing paste were used in printing pastes studying their color effect. Various printing pastes containing the zinc oxide nanoparticles and reactive dye applied to cotton fabrics using silk screen printing process. Table 1 shows the effect of zinc oxide nanoparticles concentration on some overall fastness properties and color strength of dried and steam-fixated printed fabrics.

It is clear from Fig. 5 that incorporation of zinc leads to significant enhancement in color strength (K/S). oxide nanoparticles.

The overall fastness properties of the prints are acceptable regardless of the zinc oxide nanoparticles concentration. Zinc oxide nanoparticles used to be known as photocatalytic material which can absorb UV-vis light followed by electron excitation. These exited electrons affect the resonance of color and showed positive effect on color fastness.

TABLE 1. Effect of ZnO NPs concentration on overall fastness properties and color strength of dried and steamed printed fabrics.

[ZnO] (ppm)	K/S	Washing fastness		Rubbing fastness		Perspiration fastness			
						Acidic		Alkaline	
		Alt	St	wet	dry	Alt	St	Alt	St
0	10.14	4	4-5	3-4	4	4	4-5	4-5	4-5
200ppm	10.94	4	4	4	4	4	4-5	4-5	4-5
300ppm	11.63	4	4-5	3-4	4	4	4-5	4-5	4-5
400ppm	13.54	4	4-5	3-4	4	4	4-5	4-5	4-5
500 ppm	12.30	4	4-5	4	4	4	4-5	4-5	4-5

Alt: Alteration , St: Staining on cotton.

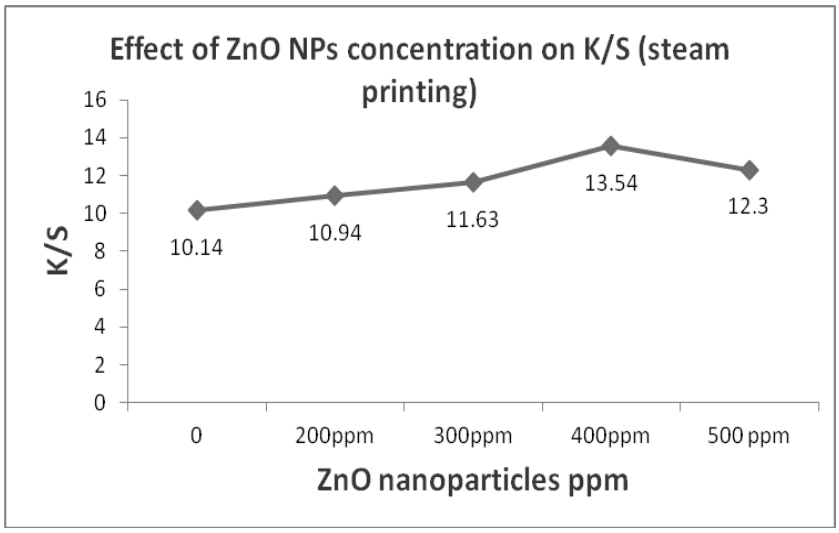

Fig. 5. Effect of ZnO NPs concentration on K/S (steam printing) .

Table 2 shows the effect of zinc oxide nanoparticles concentration on the printability of dried and thermo-fixated printed fabrics. Reactive printing with Drimarin blue P dye was carried out using different concentrations of zinc oxide nanoparticles, according to the recipe given in the Experimental section. The printed samples were assessed for color strength (K/S) and some overall fastness properties and the results obtained are summarized in Fig. 6. It is seen that by increasing zinc oxide nanoparticles concentration (with constant amount of dye) into printing paste the color strength increases significantly. On the other hand some of overall fastness properties affect positively color fastness.

TABLE 2. Effect of ZnO NPs concentration on the printability of thermo-fixated printed fabrics.

[ZnO] (ppm)	Washing fastness		Rubbing fastness		Perspiration fastness			
					Acidic		Alkaline	
	Alt	St	wet	dry	Alt	St	Alt	St
0	4	4.5	3-4	4	4	4.5	4	4.5
200 ppm	4	4.5	3-4	4-5	4	4.5	4	4.5
300ppm	4	4	4	4-5	4	4	4	4.5
400ppm	4	4.5	4-5	4-5	4	4.5	4	4.5
500ppm	4	4	4	4-5	4	4.5	4	4.5

Alt: Alteration , St: Staining on cotton

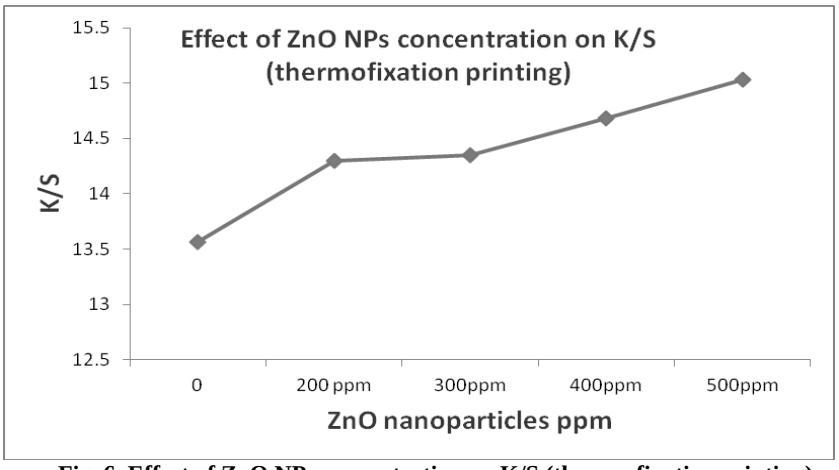

Fig. 6. Effect of ZnO NPs concentration on K/S (thermo-fixation printing).

Figure 7 shows the effect of zinc oxide nanoparticles incorporate in the printing paste on the used fixation method for the prints. This was evaluated via determining the color strength of the prints.

It is observed (Fig. 7) that the color strength (K/S) is significantly improved by thermo-fixation method regardless of the zinc oxide nanoparticles concentration. That may be because steam boiled vapor may react with zinc oxide nanoparticles forming zinc hydroxide reduced the color fastness.

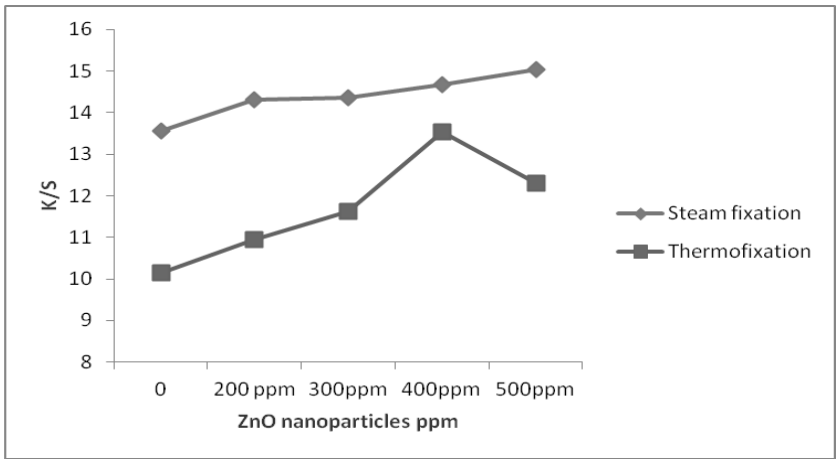

Fig. 7. Effect of ZnO NPs concentration on K/S at steam and thermo-fixation printing.

Conclusion

Zinc oxide nanoparticles are successfully prepared by alkaline precipitation. The obtained nanoparticles were deduced by spectroscopic techniques TEM and XRD. The obtained zinc oxide nanoparticles lied in nano-size between 200-300 nm. The obtained zinc oxide nanoparticle shows antibacterial activity towards microorganisms (bacteria and fungi). Zinc oxide nanoparticles affect positively color fastness of printed fabrics, especially those treated with thermo-fixation process after printing.

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تحضير جسيمات أكسيد الزنك النانومترية وتطبيقها على الأقمشة السليلوزية

محمد رمضان، سحر نصار، أحمد سعد منتصر، إيمان الخطيب و محمد عبدالعزيز*
شعبة الصناعات النسيجية و* شعبة الهندسة الوراثية والبيوتكنولوجى المركز القومى للبحوث – الجيزة – مصر.

فى هذه الدراسة تم تحضير جسيمات أكسيد الزنك النانومترية بواسطة طريقة الترسيب القاعدى بإستخدام خلات الزنك و هيدروكسيد الصوديوم كمصدر لجسيمات أكسيد الزنك. تم توصيف جسيمات الزنك النانومترية وتطبيقها على الأقمشة القطنية وإختبارها كعامل مضاد لنمو البكتيريا والفطريات بالإضافة إلى تأثيرها على عمق اللون وخواص الثبات للأقمشة المعالجة. تم إدخال جسيمات الزنك النانومترية فى عجينة الطباعة لإكساب الأقمشة خاصية المقاومة ضد نمو البكتيريا. تم توصيف شكل وحجم جسيمات أكسيد الزنك النانومترية المحضرة بواسطة جهاز الماسح الإلكترونى النافذ وجهاز حيود الأشعة السينية للمواد الصلبة. أظهرت النتائج أن حجم جسيمات أكسيد الزنك النانومترية المكونة تتراوح بين 200-300 نانوميتر للعينات المكلسنة بينما تكون أعلى من 400 نانوميتر للعينات المجففة. أوضحت النتائج أيضا أن جسيمات أكسيد الزنك النانومترية لها تأثير إيجابى تجاه الكائنات الدقيقة مثل البكتريا والفطريات. كما لها إيضا تأثير إيجابى على خواص الثبات وعمق اللون للأقمشة المطبوعة المعالجة.