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Adsorption/photo-catalytic removal of phenol using C_3N_4, CuO nanoparticle and CuO-C_3N_4 composite

I. A. S. Mansour[1], Hend M. Sharawy[1], Mona E. Ossman[2,3] and Marwa Abdelfattah[3*]

[1]Chemical Engineering Department, Faculty of Engineering, Alexandria University, Alexandria 21544, Egypt, [2]City for Scientific Research and Technology Application (CSAT), Alexandria 21544, Egypt, [3]Petrochemical Engineering Department, Pharos University (PUA), Alexandria 21544, Egypt

Abstract

Phenol is one of the major pollutants in the wastewater because of its presence in the effluent of major processing and refining plants. Phenol has severe short term and long term effect on human being due to their poor biodegradability and high toxicity. The present work explored the use of three different materials namely; CuO nano-particle, C_3N_4 and CuO-C_3N_4 composite for the removal of phenol from wastewater by adsorption and photo catalytic. The three different materials were prepared and fully characterized. The results indicated that the percentage removal of the phenol by adsorption using both CuO nano-particles and C_3N_4 are rapid in the beginning reached equilibrium within 1hr and 80 min respectively. The removal of phenol reached 63.5% and 49% by using CuO nano-particles and C_3N_4 respectively which indicated that CuO nano-particles is more efficient for phenol removal by adsorption than C_3N_4. By using the photo-catalytic method; it was found that the composite of (80% C_3N_4 and 20% CuO) gave more efficient results for removal of phenol by photo-catalysis than CuO nano-particles and C_3N_4 individually. Results showed that adsorption process is more effective for phenol removal using the three materials than the removal by photo-catalytic process. Kinetic model for the removal of phenol by adsorption and photo catalytic processes has been investigated.

Key words: Adsorption, Phenol, Photocatalytic, Wastewater Treatment

Full length article **Corresponding Author*, e-mail: marwa.abdelfattah@pua.edu.eg, Tel: 002-033877436

1. Introduction

Phenol as a manufactured chemical and a natural substance, are detected in a variety of industrial wastewaters, such as refineries, products, pesticide, paint, coking operations, coal processing, pharmaceuticals, plastics, wood and paper industries [1,2]. The presences of phenolic compounds have been documented in different mediums such as sewage sludge, influent and effluent of wastewater, river water and soil [3-6]. Phenol has a high toxic and great risk to human health and the environment. Chronic toxicity of phenols in humans results in: headache, vomiting, difficulty in swallowing, liver injury and fainting etc. [7]. Thus, the removal of phenol from wastewater is of great importance, and has been received particular concerns in the last few decades. Researchers reported different approaches for removal of phenol including enzymatic oxidation [8], chemical oxidation [9,10], catalytic oxidation [11], biodegradation [12], membrane separation [13-14], electro-coagulation [15-16], photo-catalytic [17] and many other technologies. Among various technologies, the adsorption technology considered to be the simplest and effective method which has been used extensively for the removal of phenol [18]. There are various adsorbents in use for phenol removal such as activated carbon [19-21], iron oxide [22], activated alumina [23-24]. In fact, hierarchical porous metal oxides such as copper oxide, iron oxide, aluminum oxide, titanium dioxide and others have attracted attention in adsorption applications pertaining to the uptake of toxic pollutants and heavy metals. This interest on metal oxides may often be attributed to their regular pore structures, enhanced surface areas, and controlled organization of primary building units with various dimensions into ordered nano-structures and super-structures [25-26]. In this regard, copper oxide nano-powder appears an interesting and promising transition metal oxide adsorbent, ostensibly due to its extensive applications in catalysis [27], lithium-ion batteries [28], super capacitors [29] and gas sensor [30]. Since CuO is a semiconducting material [31], so it can be used to remove organic pollutants such as phenol under UV light. The objective of this study was to investigate the use of CuO nano powder, C_3N_4 and CuO-C_3N_4 composite for the removal of phenol from wastewater by adsorption and under UV light.

2. Material and Methods

2.1 Preparation of g-C_3N_4

All chemicals for synthesis and analysis were commercially available and were used without further treatments. The graphitic C_3N_4 powder was synthesized by the thermal poly condensation of melamine. Typically, 5 g

of melamine was placed in a crucible with a cover and calcined at 500 ˚C for 4 h in a muffle furnace at a heating rate of 20 ˚C min^{-1}. The resulting yellow product was collected and ground into a powder for further use.

2.2 Preparation of CuO nano-particles

3.6 g of Cu $(NO_3)_2 \cdot 3H_2O$ (0.1 M) was dissolved in 300 ml deionized water in a round-bottom flask and then 30 ml of Di-ethylene glycol (DEG) was poured into the solution. After DEG uniformly dispersed in the solution, KOH (0.2 M) were added. The solution was vigorously stirred for 3 h then; the mixture was placed in the microwave reflux system and the reaction was carried out under ambient air for 15 min. After the reaction was completed, a great amount of dark brown precipitate occurred. After cooling to room temperature, all precipitate was filtered, and repeatedly washed by deionized water and ethanol for several times and finally dried at 80 °C for 10 h.

2.3 Preparation of C_3N_4 (80%) and CuO nano-particles (20%) composite

The prepared C_3N_4 and CuO nano-particles were mixed in a ratio 8:2 by weight and grinded in a mortal. In order to know the structure sight of the adsorbents produced, scanning electron microscopy (SEM) was employed to visualize samples morphology. The surface functional groups and structure were also studied by FTIR spectroscopy.

2.4 Batch experiments

A stock solution of phenol (1000 mg/l) was prepared by dissolving 1g of phenol in 1L of distilled water. Equilibrium isotherms for phenol were obtained by performing batch adsorption studies. Solutions of 250 ml were adjusted to optimum pH values and adsorbents amounts ranging between 0.1 and 1 g were added to solutions.

The adsorbed phenol amount (q) per unit absorbent mass was calculated as follows (Eq. 1):

$$q = \frac{(C_i - C_f)}{Wt} * V \qquad (1)$$

Where C_i is the initial phenol concentration (mg/L), C_f is the concentration of phenol at equilibrium (mg/L), Wt is the adsorbent dosage (g) and V is the solution volume (L).

2.5 Photocatalytic performance of CuO, C_3N_4 and CuO-C_3N_4 composite

Photocatalytic activity of CuO, C_3N_4 and CuO-C_3N_4 composite for phenol degradation was evaluated in a Pyrex glass beaker with the volume of 250 ml, 0.8 g C_3N_4 or CuO or CuO-C_3N_4 composite was dispersed in phenol aqueous solution, as shown in Fig. 1. Photo degradation of phenol was performed under a 300 W UV lamp with cutoff filter for visible light (256 nm).

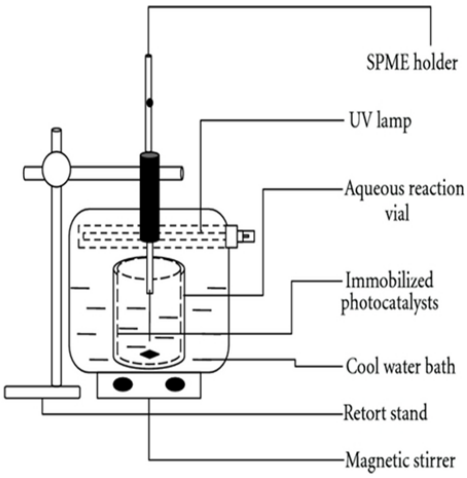


Fig.1 Apparatus design used for photocatalytic operation

2.6 Determination of phenol in the solution

The concentration of phenol in the solution was determined by using direct photometric method. Phenol concentration was measured using spectrophotometer (Spectronic 20D, Milton Roy Company). The absorbance of colored complex of phenol with 4-aminoantipyrine was found at 500 nm [32].

3. Results and Discussion

3.1 *Characterization of adsorbent*

3.1.1 Morphology and particle size

In order to understand the morphology of the adsorbent SEM analyses of CuO nano powder, C_3N_4 and CuO-C_3N_4 composite were carried out. SEM image with magnification factor 2000-3500 is presented in Fig. 2. Fig. 2-a showed the SEM for C_3N_4, the samples appeared to have aggregated particles, which contained many smaller crystals and well-crystallized C_3N_4 structures with clear hexagonal morphology and size range of 50–500 nm. While Fig. 2-b showed the rectangular morphology for CuO nano powders with high surface roughness of the particles. The increase in surface roughness leads to an increase in the surface area of the adsorbent. Fig. 2-c showed the SEM for CuO-C_3N_4 composite (80% C_3N_4 to 20% CuO) showed a mixture of hexagonal and rectangular morphology. The particle size distribution for CuO nano powder, C_3N_4 and CuO-C_3N_4 composite are presented in Table 1.

3.1.2 FTIR for C_3N_4 and CuO nano powder

The FTIR analysis permits spectrophotometric observation of C_3N_4 and CuO nano in the range 400–4,000cm^{-1} and serves as a direct means for the identification of the functional groups on the surface. Fig. 3 shows the Fourier transformed spectrum of CuO nano powders at room temperature. The characteristic peaks of CuO positioned from 984 cm^{-1} to 426 cm^{-1}. The peaks at 521 cm^{-1} and 603 cm^{-1} indicated the formation of CuO nanostructure and the vibration of Cu-O and stretching of Cu-O along the [202] direction [33] respectively. The bands at 803 cm^{-1} and 1021 cm^{-1} are due to the Cu-OH deformation. The peak at 1458

cm^{-1} is evidence of (N-O) tremble. Band at 1639cm^{-1} was representing the H-O-H bending.

The IR peak at 3436 cm^{-1} is OH stretching bands of H_2O. While in Fig. 4; there are several strong bands in the 1242 – 1638 cm^{-1} region which are the stretching modes of CN heterocyclics [34–37]. More than that, the sharp peak at 1683 cm^{-1} can be deemed as an indication of good crystallinity of g-C_3N_4. The two absorption peaks at 1300–1412 cm^{-1} and 1529–1638 cm^{-1} are assigned, respectively, to $C(sp^2)$–N (1320 cm^{-1}) and $C(sp^2)$=N (1610 cm^{-1}) stretching modes in a graphite-type structure (such a band is forbidden in the FTIR spectrum of pure graphite single crystals). Additionally, a broad band at around 3172 cm^{-1} is indicative of NH stretching vibration modes. Indeed, as reported, the residual hydrogen atoms bind to the edges of the graphene–like C–N sheet in the form of C–NH_2 and 2 C–NH bonds [38].

3.2 Effect of contact time

The effect of contact time on the removal of phenol by adsorption and photo catalytic using CuO nano and C_3N_4 powder are presented in Fig. 5(a,b) and Fig.6 (a,b and c). In Fig.5, the uptake of phenol found to be rapid in first 10 minutes and reached equilibrium after 40 minutes for both CuO and C_3N_4 nano powder respectively. The initial rapid phase may be due to the increased number of vacant sites available at the initial stage. Later, the process becomes relatively slower and equilibrium conditions are reached within 50 minutes. For 50 mg/l phenol; 95% removal has been reached within 50 min by using CuO nano powder while 73% has been reached by using C_3N_4. Removal of phenol by photo catalytic was shown in figure 6. The % removal using 80% C_3N_4 and 20% CuO (by wt.) was 45% but by using CuO nano-particles was 42.2% while by using C_3N_4 as catalyst, the % removal was 28% (50 ppm phenol and 0.8 g/l dosage of catalyst).

The effect of concentration on the equilibration time was also investigated as function of initial phenol concentration. It was found that time required to achieve a definite fraction of equilibrium adsorption is independent of initial concentration.

3.3 Effect of weight of adsorbent

The results of the experiments with varying adsorbent dosage are presented in Fig. 6 (a,b). The results revealed that with an increase in the adsorbent dosage from 0.4 to 1.2 g/L, the removal of phenol (50 mg/l) increased from 25% to 88% by adsorption process using CuO nano powder and from 17% to 21% by photocatalytic process. While the removal of phenol increased from 27% to 69% by adsorption process using C_3N_4 and from 17% to 31% by photocatalytic process. Figure 6 also shows that 17% to 41% removal of phenol can be achieved by using 20% CuO-80% C_3N_4 composite by adsorption. Table.2 shows a Comparison between different methods for phenol removal.

3.4 Regeneration of CuO nano powder

Preliminary regeneration experiments were carried out using spent CuO nano powder adsorbent using 0.1 M HCl solution. To check the efficiency of the regenerated adsorbents, CuO nano powder was washed thoroughly in distilled water and dried properly under sunlight for 24h. The regenerated adsorbents were used for adsorption of 100 ppm phenol at adsorbent dose of 0.8 g/L for a contact time of 90 min. Results showed that only about 7 % decrease in adsorption efficiency was observed.

3.4.1 Removal kinetics

Heterogeneous photo catalysis reactions are complicated processes because it is affected by many factors. The rate equation can be stated with observed rate constant (k_{obs}) as follows (Eq. 2):

$$-r_{phenol} = -\frac{dC_{phenol}}{dt} = k_{obs}\ C_{phenol}^{n} \qquad (2)$$

Where

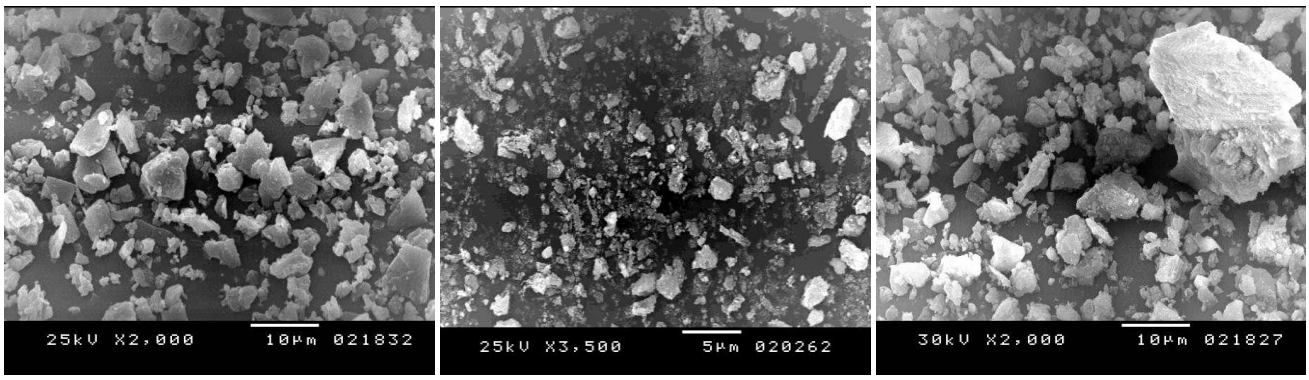
- C_{phenol} is concentration of phenol at time t (ppm)

The pseudo-first order kinetic model (n=1) provide equation 1 to the following form (Eq. 3):

$$-\ln\left(\frac{C_{phenol}}{C_{phenol\,0}}\right) = k_{obs}\ t \qquad (3)$$

Table.1 Particle size distribution for the three adsorbents

Adsorbent	Particle size distribution
C_3N_4	50-500 nm
CuO	33-110 nm
C_3N_4 (80%) + CuO (20%)	45-460



(a) (b) (c)

Fig.2 SEM for (a) C_3N_4 (b) CuO nanoparticles (c) 80% C_3N_4-20%CuO nanoparticles composite

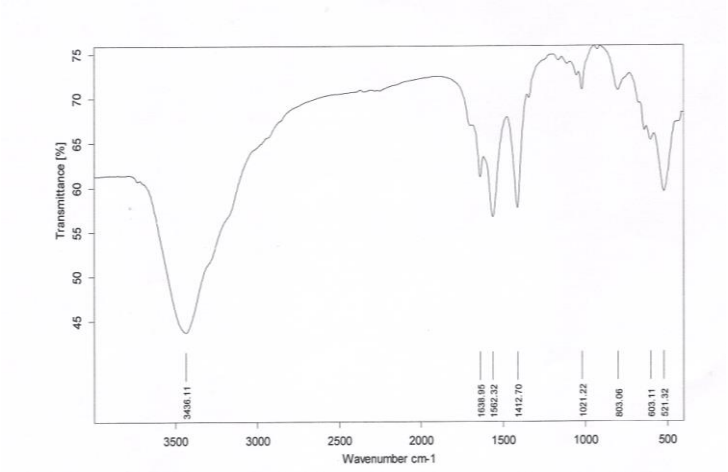


Fig.3 FTIR for CuO nanoparticles

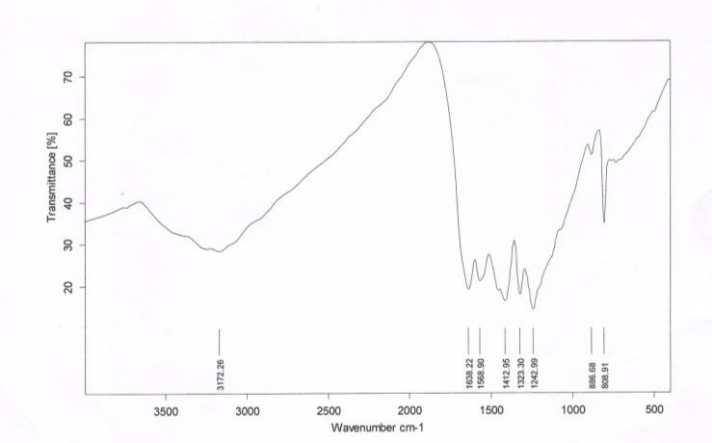
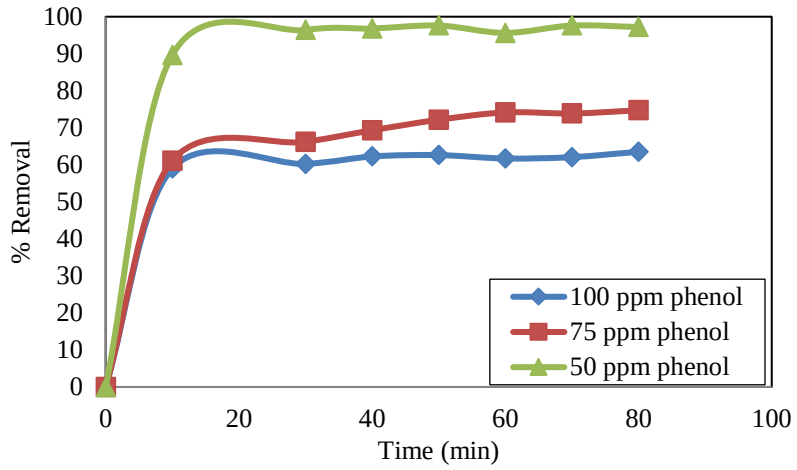
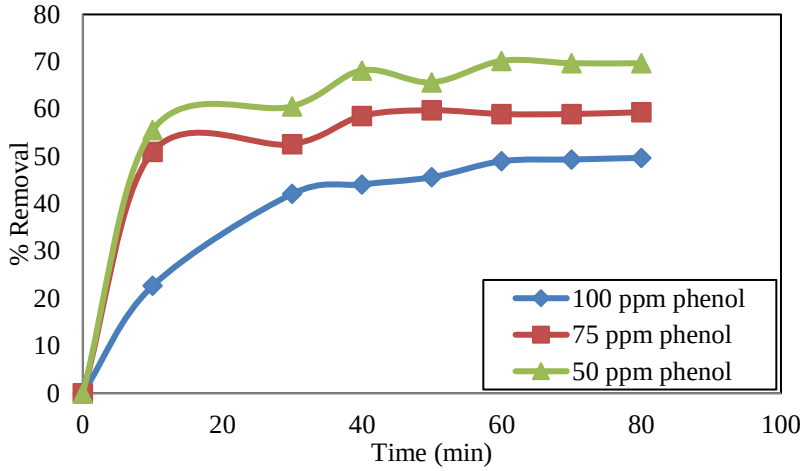


Fig.4 FTIR for C_3N_4

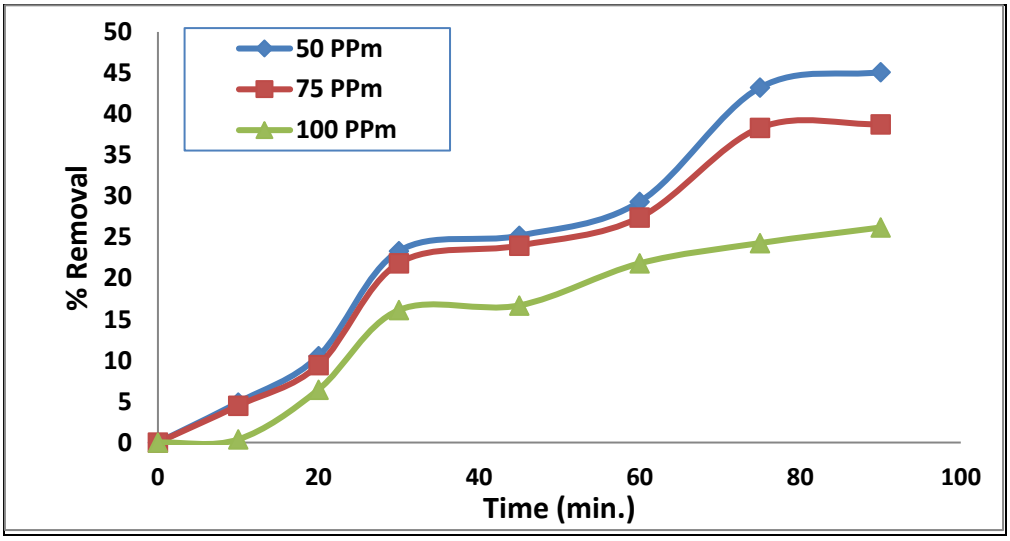


(a)

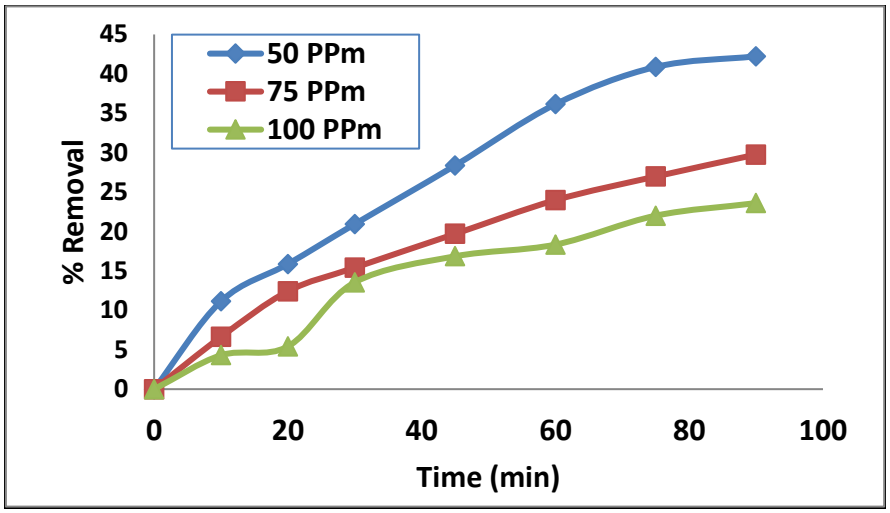


(b)

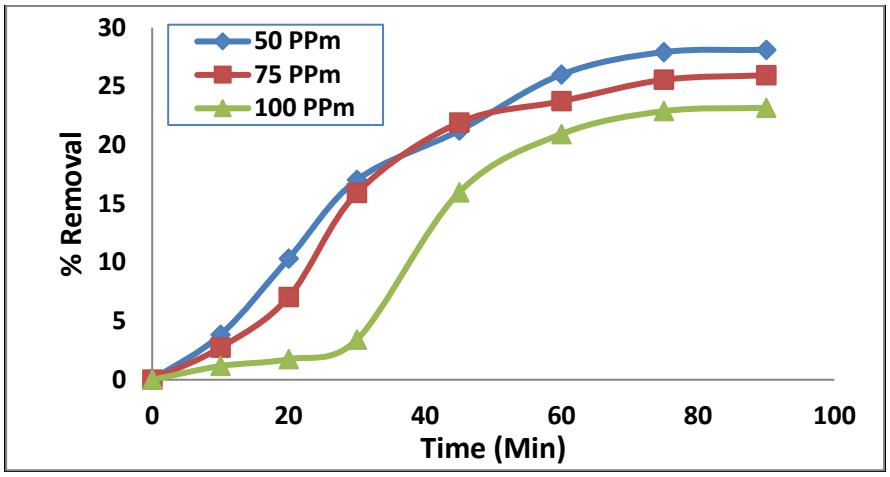
Fig.5 Effect of contact time on % removal of phenol by adsorption at different concentration using (a) CuO nano particles (b) C_3N_4 as adsorbent, adsorbent dosage 0.8 g/l and at 25°C



(a)



(b)



(c)

Fig.6 Effect of contact time on % removal of phenol at different concentration by photocatalytic process using (a) 80% by weight C_3N_4 and 20% CuO (b) CuO nano particles (c) C_3N_4 as catalyst, catalyst dosage 0.8 g/l and at 25 °C

Table.2 Pseudo first order rate constant k_{obs1} and R^2

Catalyst	k_{obs1} (1/min)				R^2			
	25 ppm	50 ppm	75 ppm	100 ppm	25 ppm	50 ppm	75 ppm	100 ppm
C_3N_4	0.0048	0.0044	0.004	0.0032	0.94	0.93	0.90	0.90
CuO	0.0086	0.0069	0.004	0.0033	0.99	0.96	0.97	0.96
80% C_3N_4 and 20% CuO	0.0109	0.0068	0.0059	0.0038	0.97	0.96	0.96	0.93

Table.3 Pseudo second order rate constant k_{obs2} and R^2

Catalyst	k_{obs1} (1/min)				R^2			
	25 ppm	50 ppm	75 ppm	100 ppm	25 ppm	50 ppm	75 ppm	100 ppm
C_3N_4	0.0002	0.0001	6E-05	4E-05	0.91	0.91	0.89	0.89
CuO	0.0005	0.0002	6E-05	4E-05	0.97	0.96	0.94	0.96
80% C_3N_4 and 20% CuO	0.0003	0.0002	8E-05	4E-05	0.93	0.95	0.96	0.95

While for pseudo-second order kinetics model (n=2) provide equation 1 to the following form (Eq. 4):

$$\frac{1}{C_{phenol}} - \frac{1}{C_{phenol\,0}} = k_{obs}\, t \qquad (4)$$

Table 2 lists of the pseudo first order rate constant k_{obs1}, and R^2 for phenol removal using the three different photo catalysts used in this study while Table 3 shows the pseudo second order rate constant k_{obs2}, and R^2. By comparing the R^2, it was found that phenol photo degradation follow pseudo first order kinetic expression by using CuO, C_3N_4, and mixture of 80% by weight C_3N_4 and 20% by weight CuO as photo catalysts.

Many reports have indicated that the kinetic model for heterogeneous photo catalysis follows the Langmuir-Hinshelwood kinetic expression [43].

$$r = -\frac{dC_{phenol}}{dt} = \frac{kK_{phenol}\,[C_{phenol}]}{1 + K_{phenol}\,[C_{phenol}]} = k_{obs}\, C_{phenol} \qquad (5)$$

$$\frac{1}{k_{obs}} = \frac{1}{kK_{phenol}} + \frac{C_{phenol0}}{k} \qquad (6)$$

In Eqs. (4) and (5), $C_{phenol0}$ is the initial phenol concentration (ppm), K_{phenol} is the Langmuir-Hinshelwood adsorption equilibrium constant (L/mg), k is the rate constant of the surface reaction (mg/L/min), and k_{obs} is the pseudo first order rate constant. According to Eq. (5), $1/k_{obs}$ versus $[C_{phenol0}]$ is a straight line and in this case the rate constant for the surface reaction of phenol degradation using 80% by weight C_3N_4 and 20% by weight CuO is k = 0.5107 (mg/L/min) and the adsorption equilibrium constant, is K_{phenol} = 0.0160 L/mg. The obtained regression coefficient R is 0.82, which suggests that the photo degradation of phenol catalyzed by 80% by weight C_3N_4 and 20% by weight CuO fits the Langmuir- Hinshelwood kinetic model.

The rate expression for photo catalytic degradation of phenol using 80% by weight C_3N_4 and 20% by weight CuO is:

$$r = \frac{0.0081 * [Cphenol]}{1 + 0.016 * [C_{phenol}]} \qquad (7)$$

While the rate constant for the surface reaction of phenol using CuO is k = 0.356 (mg/L/min) and the adsorption equilibrium constant, *K phenol* = 0.011 L/mg. The obtained regression coefficient R is 0.9788, which suggests that the photo degradation of phenol catalyzed by CuO fits the Langmuir- Hinshelwood kinetic model.

The rate expression for photo catalytic degradation of Phenol using CuO is:

$$r = \frac{0.004 * [C_{phenol}]}{1 + 0.011[C_{phenol}]} \qquad (8)$$

And the rate constant for the surface reaction of phenol using C_3N_4 is k = 0.716 (mg/L/min) and the adsorption equilibrium constant, *K phenol* = 0.004 L/mg. The obtained regression coefficient R is 0.9788, which suggests that the photo degradation of phenol catalyzed by g-C_3N_4 fits the Langmuir- Hinshelwood kinetic model.

The rate expression for photo catalytic degradation of phenol using g-C_3N_4 is:

$$r = \frac{0.008 * [C_{phenol}]}{1 + 0.016[C_{phenol}]} \qquad (9)$$

3.4.2 Regeneration of CuO nano powder

Preliminary regeneration experiments were carried out using spent CuO nano powder adsorbent using 0.1 M HCl solution. To check the efficiency of regenerated adsorbents, CuO nano powder was washed thoroughly in distilled water and dried properly under sunlight for 24h. The regenerated adsorbents were used for adsorption of 100 ppm phenol at adsorbent dose of 0.8 g/L for a contact time of 90 min. Results showed that only about 7 % decrease in adsorption efficiency was observed.

4. Conclusions

Three different materials namely; CuO nano-particle, C_3N_4 and CuO-C_3N_4 composite were prepared and fully characterized considering its chemical structure, particle size and morphology. The three materials were tested to be used for the removal of phenol from wastewater by adsorption and under UV light. The results indicated that the % removal of the phenol by adsorption using both CuO nano particles and C_3N_4 are rapid in the beginning reached equilibrium within 1hr and 80 min respectively. The removal of phenol reached 63.5% and 49% by using CuO nano particles and C_3N_4 respectively for 100 ppm phenol, 0.8 g/l of adsorbent dosage and 1hr which indicated that CuO nano particles is more efficient for phenol removal by adsorption than C_3N_4. By using the photo-catalytic method; it was found that the composite of (80% C_3N_4 and 20% CuO) gave more efficient results for removal of phenol by photo-catalysis than CuO nano particles and C_3N_4 individually. Results showed that adsorption process is more effective for phenol removal using the three materials than the removal by photo-catalytic process. The pseudo first order kinetic model provided good correlation for the removal of phenol by adsorption and photo catalytic processes.

References

[1] L. Damjanović., V. Rakić, V. Rac., D. Stošić and A. Auroux. (2010). The investigation of phenol removal from aqueous solutions by zeolites as solid adsorbents. Journal of Hazardous Materials. 184(1–3): 477-484.

[2] S.H. Lin. and R.S. Juang. (2009). Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: a review. Journal of Environmental Management. 90(3): 1336-1349.

[3] V. Niedan., J. Pavasars. and G. Oberg. (2000). Chloroperoxidase mediated chlorination of

aromatic groups in fulvic acid. Chemosphere. 41: 779-785.
[4] E. Fries. and W. Puttman. (2003). Occurrence and behaviour of 4-nonylphenol in river water of Germany. Journal of Environmental Monitoring. 5: 598-603.
[5] D. Berryman., F. Houde, C. DeBlois. and M. Oshea. (2004). Nonylphenolic compounds in drinking and surface waters downstream of treated textile and pulp paper effluents: a survey and preliminary assessment of their potential effects on public health and aquatic life. Chemosphere. 56: 247-255.
[6] E. Pocurull., R. Marce. and B. Borrull. (1996). Determination of phenolic compounds in natural waters by liquid chromatography with ultraviolet and electrochemical detection after online trace enrichment. Journal of Chromatography. 738: 1-9.
[7] H. Cherifi., S. Hanini. and F. Bentahar. (2009). Adsorption of phenol from wastewater using vegetal cords as a new adsorbent. Desalination. 244: 177-187.
[8] K.Q. Wilberg., D.G. Nunes. and J. Rubio. (2000). Removal of phenol by enzymatic oxidation and flotation. Brazilian Journal of Chemical Engineering. 14: 4-7.
[9] J.A. Zazo., J.A. Casas., A.F. Mohedano., M.A. Gilarranz. and J.J. Rodríguez. (2005). Chemical pathway and kinetics of phenol oxidation by fenton's reagent. Environmental Science and Technology. 39(23): 9295-9302.
[10] Y. Yavuz., A.S. Koparal. and U.B. Ögütveren. (2007). Phenol removal through Chemical Oxidation using Fenton Reagent. Chemical Engineering and Technology. 30(5): 583-586.
[11] M. Saeed. and M. Ilyas. (2010). Oxidative removal of phenol from water catalyzed by nickel hydroxide. Applied Catalysis B: Environmental. 129(2013): 247-254.
[12] S. Chakraborty., T. Bhattacharya., T.N. Patel. and K.K. Tiwari. (2010). Biodegradation of phenol by native microorganisms isolated from coke processing wastewater. Journal of Environmental Biology. 31(3): 293-6.
[13] Mixa. and C. Staudt. (2008). Membrane Based Separation of Phenol/Water Mixtures Using Ionically and Covalently Cross Linked Ethylene Methacrylic Acid Copolymers. International Journal of Chemical Engineering. 1-12.
[14] W. Kujawski., A. Warszawski., W. Ratajczak., T. Porębski., W. Capała. and I. Ostrowska. (2004). Removal of phenol from wastewater by different separation techniques. Desalination. 163: 287-296.
[15] O. Abdelwahab., N.K. Amin. and E.S. El-Ashtoukhy. (2009). Electrochemical removal of phenol from oil refinery wastewater. Journal of Hazardous Materials. 163(2-3): 711-6.
[16] M.E. Olya. and A. Pirkarami. (2013). Electrocoagulation for the removal of phenol and aldehyde contaminants from resin effluent. Water Science and Technology. 68(9): 1940-9.
[17] C.H. Chiou. and R.S. Juang. (2007). Photocatalytic degradation of phenol in aqueous solutions by pr-doped TiO_2 nanoparticles. Journal of Hazardous Materials. 149(1): 1-7.
[18] M. Ahmaruzzaman (2008). Desorption of phenolic compounds on low-cost adsorbents: a review. Advances in colloid and interface science. 143(1–2): 48-67.
[19] T. Y. Kim., H. J. Jin., S. S. Park., S. J. Kim. and S. Y. Cho. (2008). Adsorption equilibrium of copper ion and phenol by powdered activated carbon, alginate bead and alginate-activated carbon bead. Journal of Industrial and Engineering Chemistry. 14(6): 714-719.
[20] N. Tancredi., N. Medero., F. Möller., J. Píriz., C. Plada. and T. Cordero. (2004). Phenol adsorption onto powdered and granular activated carbon, prepared from Eucalyptus wood. Journal of Colloid and Interface Science. 279(2): 357-363.
[21] J. Fan., J. Zhang., C. Zhang., L. Ren. and Q. Shi. (2011). Adsorption of 2,4,6-trichlorophenol from aqueous solution onto activated carbon derived from loosestrife. Desalination. 267(2–3): 139-146.
[22] H. Tavallali. and M. Shiri. (2012). Solid Phase Extraction of Phenol from Wastewater by Magnetic Iron Oxide Nanoparticles. International Journal of ChemTech Research. 4(1): 311-318.
[23] J. Sabeeh., W. Hassan. and M. Hamad. (2011). Adsorption study of some derivatives of phenols on activated alumina in aqueous solution. Diyala Journal for pure sciences. 2: 77-82.
[24] Zhu Li-Nan, Ma Jun and Yang Shi-Dong (2007). Removal of phenol by activated alumina bed in pulsed high voltage electric field. Journal of environmental sciences. 10: 409-415.
[25] Henglein. (1989). Small particle research – physicochemical properties of extremely small colloidal metal and semiconductor particles. Chemical Reviews. 89: 1861-1873.
[26] M.A. El-Sayed. (2001). Some interesting properties of metals confined in time and nanometer space of different shapes. Accounts of Chemical Research. 34: 257-264.
[27] P.D. Wei., P.W. Yu. and J.H. Ta. (1996). Yttria-Stabilized Zirconia Supported Copper Oxide Catalyst: I. Effect of Oxygen Vacancy of Support on Copper Oxide Reduction. Journal of Catalysis. 160(2): 155–170.
[28] P. Huan., D.B. Jiawei., M. Yahui., L. Guochang., A. Yaning., C. Jing., Z. Jiangshan., Z. Honghe. and D. Jimin. (2012). Cupric Oxide Nanorods on Double Face Copper Micro puzzles Electrode as Promising Anode Materials for Lithium Ion Batteries. International Journal of Electrochemical Science. 7: 10735-10747.
[29] V.D. Patake., S.S. Joshi., C.D. Lokhande. and J. Oh-Shim. (2009). Electrodeposited porous and amorphous copper oxide film for application in super capacitor. Materials Chemistry and Physics. 114(1): 6-9.
[30] Rydosz. (2013). Nano-thin CuO films doped with Au and Pd for gas sensors applications,

Informatics, Electronics and Vision (ICIEV). International Conference. 1-5.
[31] R. Ahmad. and G. Mehrnaz. (2012). Preparation and properties of semiconductor CuO nanoparticles via a simple precipitation method at different reaction temperatures. Optical and Quantum Electronics. 44: 313-322.
[32] APHA, AWWA and WEF (1998). Standard methods for the examination of water and wastewater, 20th edition, Washimgton D.C.
[33] A.D. Mushtaq., H.N. Sang., S.K. Youn. and B.K. Won. (2010). Synthesis, characterization and electrochemical properties of self-assembled leaf-like CuO nanostructures. Journal of Solid State Electrochemistry. 14(9): 1719-1726.
[34] T. Komatsu. (2001). "Prototype carbon nitrides similar to the symmetric triangular form of melon. Journal of Materials Chemistry. 11: 802-805.
[35] T. Komatsu. (2001). "Attempted chemical synthesis of graphite-like carbon nitride". Journal of Materials Chemistry. 11: 799-802.
[36] T. Komatsu. (2001). "The first synthesis and characterization of cyameluric high polymers". Macromolecular Chemistry and Physics. 202: 19-25.
[37] X.F. Li., J. Zhang. and L.H. Shen. (2009). "Preparation and characterization of graphitic carbon nitride through pyrolysis of melamine". Applied Physics A: Materials Science & Processing. 94: 387-392.
[38] D.E. Kritikos., N.P. Xekoukoulotakis., E. Psillakis. and D. Mant-zavinos. (2007). Photocatalytic degradation of reactive black 5 in aqueous solutions: Effect of operating conditions and coupling with ultrasound irradiation. Water Research. 41: 2236-2246.
[39] Bódalo., J.L. Gómez., E. Gómez., J. Bastida. and M.F. Máximo. (2006). Comparison of commercial peroxidases for removing phenol from water solutions. Chemosphere. 63(4): 626-632.
[40] S.P. Pajooheshfar and M. Saeedi. (2009). Adsorptive removal of phenol from contaminated water and wastewater by activated carbon, almond and walnut shells charcoal. Water Environment Research. 81(6): 641-8.
[41] A.I. Mustafa., S. Alam., N. Amin., N.M. Bahadur. and A. Habib. (2008). Phenol Removal from Aqueous System by Jute Stick. Pakistan journal of analytical & environmental chemistry. 9(2): 92-95.
[42] F. Shahrezaei., A. Akhbari. and A. Rostami. (2012). Photodegradation and removal of phenol and phenolic derivatives from petroleum refinery wastewater using nanoparticles of TiO_2, International Journal of Energy and Environment. 3(2): 267-274.
[43] E.I. Morales., R. Sham., Cornejo and Farfan torres. (2012). Kinetic Studies of Photocatalytic Degradation of Tartrazine. Latin American Applied Research. 42: 45-49.