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Photocoupling of Ag_3PO_4-$Ag_2CO_3$with molecularly imprinted Polymer for enhanced removal of phenol under solar light:Application of Taguchi method

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Abstract

In the current study, photocoupling of Ag_3Po_4-$Ag_2CO_3$with molecularly imprinted Polymerwas synthesized and characterizedby XRD, FTIR and SEM analysesunder sun light. The results suggested theapplication of the synthesized photocatalyst inphotocatalytic degradation of phenol was studied using the Taguchimethod and the chosen parameters were as follows: pH (2–9), concentration(50–300 mg/l), solar light radiation time (30–180 min), and catalyst dosage (0.5–3.5 g/l).The results indicate that the optimum dosage ofthe catalyst 1.5 g/l, pH =9, phenol concentration = 50 mg/l, and irradiation time = 120 min, and the phenol removal efficiencyreached up to 73.9 % at these optimal conditions.

Keywords: Molecularly imprinted Polymer, phenol, photocatalytic efficiency, Ag_3Po_4-Ag_2CO_3, heterogenous catalyst

INTRODUCTION

Molecular imprinting polymer (MIP) is a well-known technique to generate highly selective synthetic polymer receptors for target molecules. Recently, Multifunctional composite materials prepared from different functional elements have attracted great interest because of their many practical applications. Combining MIPs with inorganic nanoparticles can lead to new chemical sensors [1−3], high efficiency photocatalysts, [4,5] and magnetic adsorbents useful for fast molecular separation [6−8]. Because of their synthetic accessibility, molecularly imprinted polymer (MIP) is ideal building blocks for preparing multifunctional composites. Formation of a heterojunction (or interface) over two semiconductors has already proven to be an effective way to improve photocatalytic activity or stability, according to previous reports. Theoretically, when a p-type semiconductor and n-type semiconductor form a p–n junction, a strong inner electric field will be formed near the junction, pointing from n toward p, owing to the arrangement of the high concentrations of negatively and positively charged ions. The difference of the electric potential in the electric field can enhance the separation of photogenerated electrons and holes, increasing the quantum efficiency of the photocatalytic reactions [9–12]. The p–n junction photocatalysts, have been shown to exhibit a high photocatalytic efficiency compared with other heterojunctions. Therefore, Ag_2CO_3, as a p-type semiconductor, can form a p–n heterojunction with Ag_3PO_4, which is an n-type semiconductor. Phenolic pollutants are toxic in nature. Their presence can be commonly observed in the streams of various industrial wastewaters [13, 14]. The presence of phenolic compounds represents a serious potential hazard for human health and aquatic life, and that is why phenols have been registered as a priority pollutant by the US Environmental Protection Agency (USEPA) [15] with a permissible limit of 0.1 mg/l in wastewater [15, 16]. In this work, we developed a general photocoupling chemistry to enable simple conjugation of MIP with inorganic catalyst. The photocatalytic activity of the material was evaluated by phenol degradation under solar light irradiation and different conditions.

EXPERIMENTAL SECTION

Photocatalyst synthesis of Ag_3PO_4-Ag_2CO_3

All chemicals were of analytical grade purity and used without furtherpurification. Briefly, 252 mg $NaHCO_3$ and 312 mg $NaH_2PO_4 \cdot 2H_2O$ were dissolved in 80 mL deionized water understirring. Then, 40 mL $AgNO_3$ aqueous solutions (approximately0.3 mol/L) was added dropwise to the solution under stirring.The precipitate was collected by centrifugation, washed threetimes with deionized water after stirring for 12 h and dried inair at 70 °C for 12 h to yield the 40%-Ag_3PO_4-Ag_2CO_3compositephotocatalyst (40 mol% Ag_3PO_4 and 60 mol% Ag_2CO_3).

Preparation of molecular imprinted polymer (MIP/Ag_2PO_4-Ag_2CO_3)

A typical procedure for preparing MIP is as following: 0.15 g phenol (1 mmol)and 0.12g styrene were dissolved in 10 mL of dichloromethane with 0.1 g of dispersed Ag_2PO_4-Ag_2CO_3 and stirred for 4 hours. Then 2.93 g EGDMA and 0.122 g benzoyl peroxide were added to the solution under nitrogen atmosphere. After hyper acoustic mixing, the mixture was then polymerized overnight by thermal initiation at 80°C, free phenol in the

formed polymer was continuously extracted and washed with methanol/acetic acid solution (9:1, v/v) until no phenol was detected by HPLC Instrument,phenol free MIP was washed by water, dried overnight and kept for further investigation. The resultant polymer was coded as MIP/ Ag_3PO_4-Ag_2CO_3.

Design of experiments (DOE)

In order to photodegrade phenol, the Taguchi method, a powerful tool for design of experiments, wereapplied to determine the optimum number of the experiments [17]. This method has been used by other researchers for statistical analysis in advanced oxidation processes [18]. This technique includes data transformation to a signal-to-noise (S/N) ratio, which is a measure of the variations presented, and the larger the S/N ratio, the more important the factors and the better the results [19]. In this paper for evaluating the performance of synthesized catalyst,determining optimum operational conditionwe used the Taguchi method in which initial pH value of the phenol solution, concentration, dosage of the catalyst, and irradiationtime are considered as the effective parameters. The factors andtheir assigned levels are presented in Table (1).The photocatalytic experiments were performed using solutions of phenol at different initial pH values (2–9), concentrations (50–300 mg/l),solar light radiation time (30–180 min), and catalyst dosage (0.5–3.5 g/l).

Table 1: Factors and their levels for design of experiments

Variables		Levels			
		1	**2**	**3**	**4**
1	**pH**	2	5	7	9
2	**Dose (g/l)**	0.5	1.5	2.5	3.5
3	**Conc.(mg/l)**	50	100	250	300
4	**Time (hr)**	2	3	4	6

For analysis of the results andoptimization of the conditions, Minitab software (Version 17) was used and theefficiency of photocatalytic reaction was reported as % degradation.

Table 2: Experimental layout for using the L16OA and experimental result for phenol removal

Run No.	**pH**	**Dose g/l**	**Conc. mg/l**	**Time hr**	**%degradation**	**S/N ratio**
1	2	0.5	50	2	70.00	36.9020
2	2	1.5	100	3	68.78	36.7492
3	2	2.5	250	4	71.78	37.1201
4	2	3.5	300	6	67.00	36.5215
5	5	0.5	100	4	71.90	37.1346
6	5	1.5	50	6	70.00	36.9020
7	5	2.5	300	2	68.00	36.6502
8	5	3.5	250	3	67.00	36.5215
9	7	0.5	250	6	67.80	36.6246
10	7	1.5	300	4	69.00	36.7770
11	7	2.5	50	3	71.94	37.1394
12	7	3.5	100	2	70.40	36.9515
13	9	0.5	300	3	69.00	36.7770
14	9	1.5	250	2	73.9	37.3729
15	9	2.5	100	6	68.90	36.7644
16	9	3.5	50	4	69.00	36.7770

For each experiment, a solution of the phenol with desired concentration was prepared,and after adjusting the pH value, it was injected into the reactor chamber along with theneeded dosage of the catalyst (according to the Taguchi table). The pH of the solutionswas adjusted on desired values using HCland NaOHdiluted solutions with the aid of pH meter. After the reactionperiod was over, the resulting solution was analyzed by the HPLC.In order to monitor the phenol concentration, samples of the solution were taken outof the reactor after the reaction time and the photocatalyst particles were filtered andseparated after a 10 min centrifugation process at 5000 rpm in a centrifuge.The degree of photodegradation(efficiency) as a function of time, which demonstrates the efficiency ofthe experiment, could be calculated with the following equation:

$$RE = \left(\frac{C_{o-C_e}}{C_o}\right) \times 100 \qquad (1)$$

Where C_o and Ce (mg/l) are the initial and final phenol concentrations, respectively.

RESULTS AND DISCUSSION

Characterization of the catalyst

The crystallographic structures of the as-prepared samples were examined by X-ray powder diffraction (XRD). As shown in Fig (1) X-ray of the Ag_3PO_4-Ag_2CO_3samples. The peaks at 18.5° (020), 20.6° (110), 32.6° (–101),33.7° (–130), 37.1° (040) and 39.6° (031) are indexed to that ofmonoclinic Ag_2CO_3 (JCPDS 01-073-4385)Further, the crystallite size was calculated using Scherrer's formula for the high intensity peak, the estimated grain size was found to be 87 nm with d-spacing 0.227 nm. The peaks at 21.0° (110),29.8° (200), 33.4° (210), 36.7° (211), 47.9° (310), 52.8° (222),55.1° (320) and 57.4° (321) are indexed to that of cubic Ag_3PO_4 (JCPDS 00-006-0505), the estimated grain size was found to be 81.95 nm with d-spacing 0.16 nm., the diffraction peaks of both Ag_3PO_4 andAg_2CO_3 can be observed in the MIP/Ag_3PO_4-Ag_2CO_3composite polymer samples but with low intensity compared to the catalyst alone.

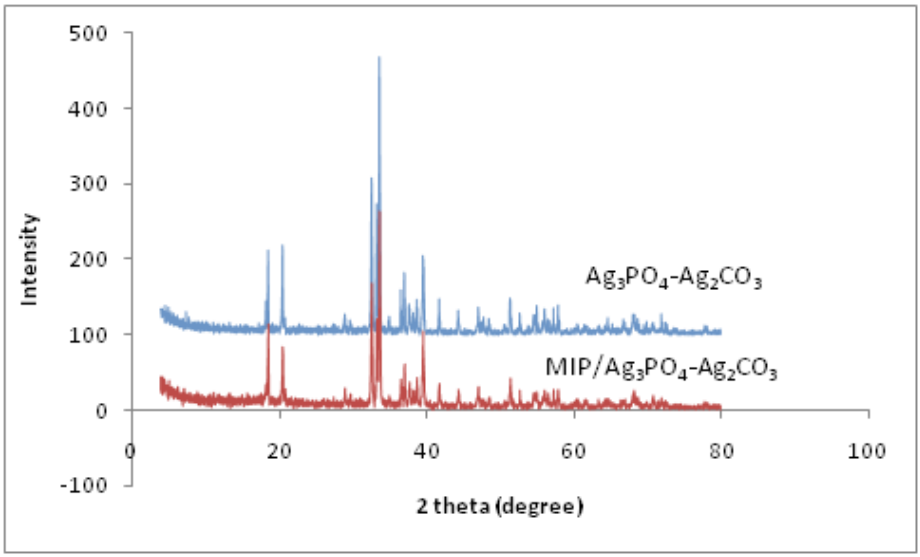


Figure 1: XRD patterns of prepared catalyst

InFT-IR spectrum of Ag_3PO_4-Ag_2CO_3Fig (2) absorption peaks at 567 and 1016 cm^{-1} can be attributed to thestretching vibrations of the PO_4group[20] which verify the existenceof Ag_3PO_4 in the sample, and the peaks around 1600 and3200 cm^{-1} represent the physically adsorbed water on thecatalyst surface.the characteristic absorptionbands of CO_3^{-2} could be observed at 708 cm^{-1}, 802 cm^{-1}, 883cm^{-1}, 1328 cm^{-1} and 1449 cm^{-1}[21]. Besides, the peaks at 1640cm^{-1} and 1540 cm^{-1} are found and the peak intention of CO_3^{2-}. The IR peaks at 1140 and 1730 cm^{-1} corresponds to C–O and C=O in EGDMA, respectively in case of MIP/Ag_3PO_4-Ag_2CO_3.The original cross-linking agent EGDMA and styrene have abundant vinyl groups. However, the characteristic C=C peaks at 1630, 990, and 910 cm^{-1} show low intensity that verified the crosslinking polymerization reaction. After surface grafting, a new vibrational peak appears in the polymer sample around 2990-2995 cm^{-1} belongs to aliphatic C–H stretching vibration. Additionally, flexions at 700–1000 cm^{-1} corresponding to aromatic C–H bond can be seen in the spectra. Peaks observed at 1313, 1185 and 1046 cm^{-1} related to the =C–H in-plane vibration and the =C–H out-of-plane vibration is found at 617 and 918 cm^{-1}. Data strongly confirms the formation hydrogen-bonding interactions between imprinted polymer and phenol molecule.

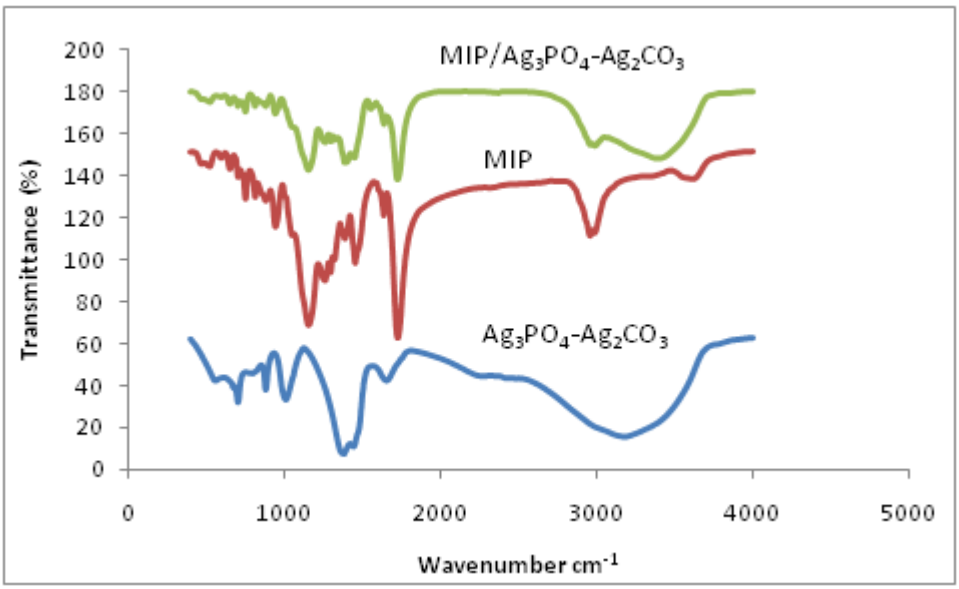


Figure 2: FTIR curves of the prepared materials

Formation of specific cavities into polymer matrix loaded with Ag_3PO_4-Ag_2CO_3plays an important role in the selective reorganization and photodegradation of phenol. The surface morphology of free and loaded polymer was examined using scanning electron microscopy. SEM images Fig. 3 (A) show particles with a polyhedral morphology similar to rhombic dodecahedral particles of Ag_3PO_4-Ag_2CO_3.Irregular shapes were found in the prepared molecular imprinting material (MIP) Fig. 3 (B) has abundant pores on the coarse surfacewith Ag_3PO_4-Ag_2CO_3deposited on the surface of polymer Fig. 3 (C).

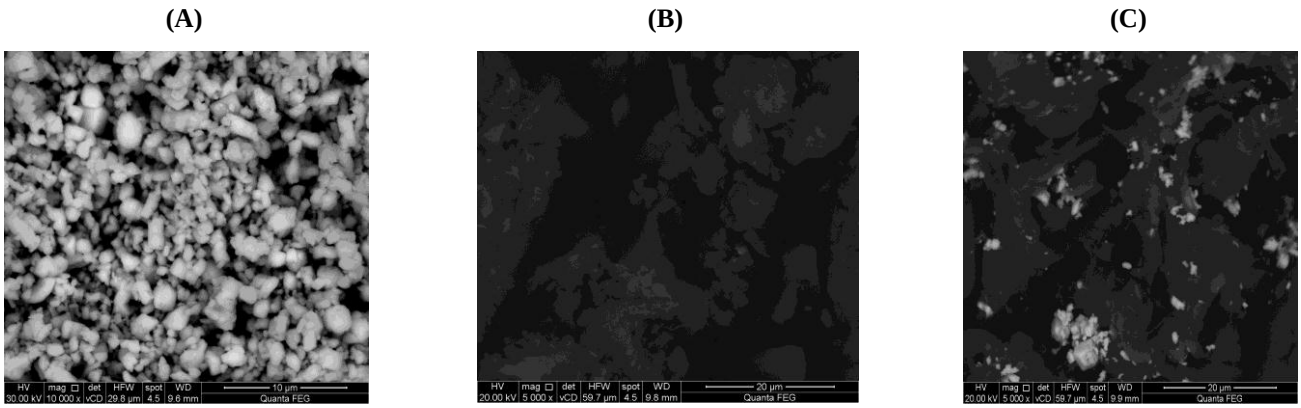


Figure 3: SEM images of (A) Ag_3PO_4-Ag_2CO_3 (B) IMP (C) IMP/ Ag_3PO_4-Ag_2CO_3

Photocatalytic activity

Taguchi orthogonal array L_{16} shows the effect of pH, dose, concentration and time on the photocatalytic activity of Ag_3PO_4-Ag_2CO_3 on to imprinted polymerusing simulatedsunlight irradiation for phenol degradation.Solar irradiation plays an important role in thephotocatalytic process in order to generate hydroxylradicals, the removal efficiency of phenol was recorded only 10% without exposure to thesolar irradiation. The removal of phenol was due tothe adsorption mechanism on the surface of Ag_3PO_4-Ag_2CO_3 and beside the cavity of polymer.

The obtainedresults after elapsing the desired irradiation time are presented in Table(2). Theoptimum value for each parameter was as follows: pH = 9, phenol concentration= 50 mg/l, catalyst dosage = 1.5g/l and solar light time = 120 min.

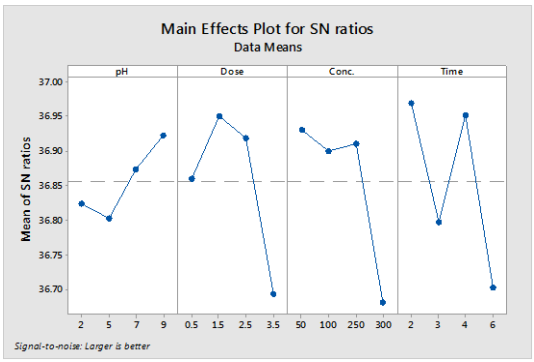


Figure 4: Response table for mean S/N ratios of MIP/Ag_3PO_4-Ag_2CO_3 for phenol degradation

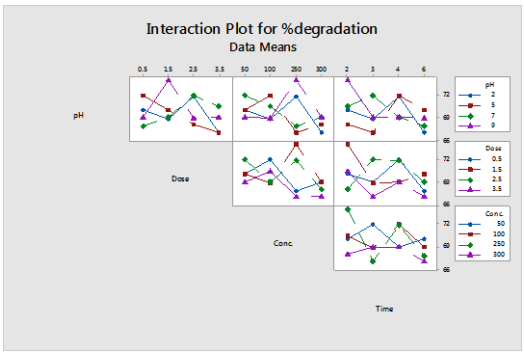


Figure 5: Interaction plot ofMIP/Ag_3PO_4-Ag_2CO_3 for phenol degradation

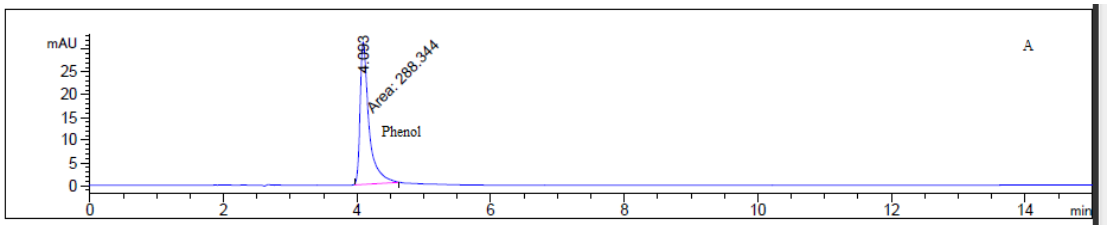
The initial concentration of organic pollutants in contaminated water is asignificant parameter that affects the efficiency of the treatment process [23]. Results also showthat as the initial phenol concentration was increased from 50 to 300 mg/L, thedegradation efficiency decreased, this phenomenon is dueto the decrease in the relative ratio of the hydroxyl radicals to the molecules of theorganic contaminants in the solution as suggested by Hashim et al. [24]. Theyfurther stated that when the concentration of the pollutant increases, the amount ofthe molecule adsorbed onto the surface of the catalyst also increases resulting infewer cavities bind with the recognition sites. Also, as the concentration of the compoundincreases, the solution becomes more turbid thereby reducing the amount ofphotons that get to the catalyst surface and as a result, the amount of hydroxylradicals attacking the organic molecules becomes limited thus reducing thedegradation efficiency [25, 26].

Fig(4) and confirmed by sever interaction between these factors as shown in Fig (5) shows the effect of catalyst loading on the photodegradation process. Theresults show that the percentage of phenol degraded increased with increasingcatalyst loading up to 1.5g/L of MIP/Ag_3PO_4-Ag_2CO_3 and thereafter decreased with increasing MIP/Ag_3PO_4-Ag_2CO_3loading. Thedecrease in degradation efficiency observed beyond a catalyst loading of 1.5 g/Lcould be attributed to the increase in the turbidity of the solution as a result of theexcess catalyst present in the degradation reaction vessel. This leads to the so calledscreening effect that involves the reflectance, interception and scattering of light andhence a fraction of the available light rays do not penetrate into the solution [29]. A similar behavior was observed by Hashim et al. [24] who reported that inbatch or dynamic flow photoreactors, the initial reaction rates are directlyproportional to the catalyst loading indicating a true heterogeneous catalytic regime,but above a certain loading limit, the reaction rate levels off and further increase incatalyst loading does not benefit the process. So et al. [30] suggested thatagglomeration and sedimentation of the catalyst particles at high catalyst loadingcould also be responsible for the decrease in degradation efficiency.

During optimization of the removal of phenol, all factors affecting the activity of should be considered, particularly pH which is the most important factor, the concentration of free phenoxide ions and OH^- is expected to increase as solution becomesmore basic. It is evident fromthe Fig. (4) That removal of phenol by MIP/Ag_3PO_4-Ag_2CO_3 was lower at acidic pH, due to pH below 7, a significantly high electrostatic attraction exists between the positively changed surface and phenolate ion ($C_6H_5O^-$) similar observation was reported by Nabais et al, [22].

The optimum contact time is 120 minunder sunlight recorded 73.9 % removal. It is reasonable toassume that the surface of MIP/Ag_3PO_4-Ag_2CO_3hasmuch imprinted cavities, the template phenol was easyto enter into the cavities and bind with the recognitionsites. When the recognition sites were filled up,the rate of adsorption dropped significantly andadsorption process achieved equilibrium gradually.

Phenol oxidation process is accompanied with evolution of several aromatic intermediates,data obtained from high performance liquid chromatography Fig (6) show benzoquinone, hydroquinone, catechol and phenol.



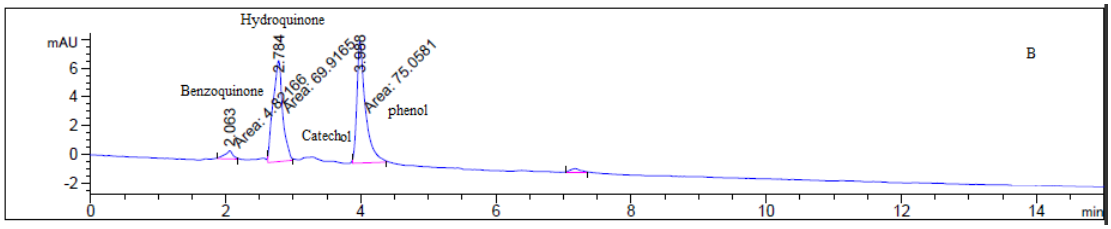


Figure 6: HPLC chromatogram of phenol (a) before and (b) after degradation under sunlight.

Implementation of ANOVA

In order to conduct an analysis of the relative importance of each factor more systematically, an ANOVA was applied to the data. The main objective of ANOVA is to extract from the results how much variations each factor causes relative to the total variation observed in the result [32]. The results of ANOVA are listed in Table (3), degree of freedom for the error is 3. According to the results, the F-ratio (0.11) for pH is smaller than the F-Ratio for dose (0.49), concentration (0.51 and time (0.61). This means that the variance in pH is insignificant compared with the variance in dose and concentration that has a significant effect on the responses. Quantitative evaluation can be achieved using percentage contribution (P%) [33]. Percent contributions of all factors are presented in Table (3). The order of importance of factors is as follows: Time>Concentration > dose > pH.

Table3: ANNOVA Table

Source	Degree of freedome	Sum of squares	Mean of squares	F-value	P-value	Percentage contribution =ss/ss(tota)*100
pH	3	2.276	0.7586	0.11	0.949	3.8
Dose	3	10.154	3.3847	0.49	0.715	18
Concentration	3	10.569	3.5229	0.51	0.704	18.7
Time	3	12.680	4.2267	0.61	0.653	22.48
Error	3	20.812	6.9372			
Total	15	56.390				

CONCLUSIONS

In this research, application of photocoupling of Ag_3PO_4-Ag_2CO_3 with molecularly imprinted polymer (MIP/Ag_3PO_4-Ag_2CO_3) for enhanced removal of phenol under solar light was investigated. The results indicate that the phenol concentration, pH, dose and solar light radiation time are respectively the most effective factors in these experiments. Considering the efficiency of the degradation process was significantly high even by using small quantities of this photocatalyst. With regard to the above-mentioned facts this method can be assumed as an applicable way to remove phenol from wastewaters.

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REFERENCES

[1] Zhao Y, Ma Y, Li H, Wang L. Anal. Chem. 2012;84:386–395. [PubMed]

[2] Matsui J, Akamatsu K, Nishiguchi S, Miyoshi D, Nawafune H, Tamaki K, Sugimoto N. Anal. Chem. 2004;76:1310–1315. [PubMed]

[3] Tokonami S, Shiigi H, Nagaoka T. Anal. Chim. Acta. 2009;641:7–13. [PubMed]

[4] Xu L, Pan J, Xia Q, Shi F, Dai J, Wei X, Yan Y. J. Phys. Chem. C. 2012;116:25309–25318.

[5] Zhang W, Li Y, Wang Q, Wang C, Wang P, Mao K. Environ. Sci. Pollut. Res. Int. 2013;20:1431–1440. [PubMed]

[6] Gonzato C, Courty M, Pasetto P, Haupt K. Adv. Funct. Mater. 2011;21:3947–3953.

[7] Liu Y, Huang Y, Liu J, Wang W, Liu G, Zhao R. J. Chromatogr. A. 2012;1246:15–21. [PubMed]

[8] Lu C-H, Wang Y, Li Y, Yang H-H, Chen X, Wang

X-R. J. Mater. Chem. 2009;19:1077–1079.

[9] Yu C L, Zhou W Q, Yu J C, Liu H, Wei L F. *Chin J Catal.* 2014, 35: 1609

[10] Wang H L, Zhang L S, Chen Z G, Hu J Q, Li S J, Wang Z H, Liu J S, Wang X C. *Chem. Soc. Rev*, 2014, 43, 5234

[11] Moniz S J A, Shevlin S A, Martin D J, Guo Z X, Tang J W. *Energy Environ Sci,* 2015, 8: 731

[12] Zhang J S, Zhang M W, Sun R Q, Wang X C. *Angew Chem. Int. Ed,* 2012, 51: 10145

[13] Cao S, Chen G, Hu X, Yue PL (2003) Catalytic wet air oxidation of wastewater containing ammonia and phenol over activated carbon supported Pt catalysts. Catalysis Today 88:37–47

[14] Jiang H, Fang Y, Fu Y, Guo QX (2003) Studies on the extraction of phenol in wastewater. J Hazard Mater B 101:179–190

[15] United States Environmental Protection Agency (USEPA) (1985) Technical support document for water quality based toxics control: EPA/440/485032. USEPA, Washington, DC

[16] Srivastava VC, Swamy MS, Mall ID, Prasad B, Mishra IM (2006) Adsorptive removal of phenol by bagasse fly ash and activated carbon: equilibrium, kinetics and thermodynamics. Colloid Surf A 272:89–104

[17] G. Taguchi, Introduction to Quality Engineering: Designing Quality into Products and Processes, Asian Productivity Organization, Tokyo, 1986.

[18] J. Zolgharnein, N. Asanjrani, M. Bagtash, G. Azimi, Multi-response optimization using Taguchi design and principle component analysis for removing binary mixture of alizarin red and alizarin yellow from aqueous solution by nano c-alumina, Spectrochim. Acta, Part A 126 (2014) 291–300.

[19] Z. BerilGo¨nder, Y. Kaya, I. Vergili, H. Barlas, Optimization of filtration conditions for CIP wastewater treatment by nanofiltration process using Taguchiapproach, Sep. Purif. Technol. 70 (2010) 265–273.

[20] N. Mohaghegh, E. Rahimi and M. R. Gholami, Mater. Sci. Semicond. Process., 2015, 39, 506–514.

[21] Y. X. Song, J. X. Zhu, H. Xu, C. Wang, Y. G. Xu, H. Y. Ji, K. Wang, Q. Zhang and H. M. Li, J. Alloys Compd., 2014, 592, 258–265.

[22] Nabais, J.M.V., Suhas J.A.G., Carrott, Laginhas, P.J.M., and Roman, C., S., Phenol removal onto novel activated carbons made from lignocellulosic precursors: influence of surface properties, J. Hazard. Mater., (2009), vol. 16, pp: 904–910.

[23] Hong, S.S.; Ju, C.S.; Lim, C.G.; Ahn, B.H.; Lim, K.T.; and Lee, G.D. (2001). A photocatalytic degradation of phenol over TiO2 prepared by sol-gel method. Journal of Industrial and Engineering Chemistry, 7(2), 99-104.

[24] Hashim, H.A.A.; Mohamed, A.R.; and Lee, K.T. (2012). Solar photocatalytic degradation of tartrazine using titanium dioxide. JurnalTeknologi, 35(1), 31-40.

[25] Akyol, A.; Yatmaz, H.C.; and Bayramoglu, M. (2004). Photocatalyticdecolorization of remazol red RR in aqueous ZnO suspensions. Applied Catalysis B: Environmental, 54(1), 19-24.

[26] Byrappa, K.; Subramani, A.K.; Ananda, S.; Rai, K.L.; Dinesh, R.; and Yoshimura, M. (2006). Photocatalytic degradation of rhodamine B dye using hydrothermally synthesized ZnO. Bulletin of Materials Science, 29(5), 433-438.

[27] Akpan, U.G.; and Hameed, B.H. (2009). Parameters affecting thephotocatalytic degradation of dyes using TiO2-based photocatalysts: Areview. Journal of Hazardous Materials, 170(2-3), 520-529.

[28] Inamdar, J.; and Singh, S.K. (2008). Photocatalytic detoxification method forzero effluent discharge in dairy industry: Effect of operational parameters.International Journal of Chemical and Biological Engineering, 1(4), 160-164.

[29] Saquib, M.; Tariqa, M.A.; Faisala, M.; and Muneer, M. (2008).Photocatalytic degradation of two selected dye derivatives in aqueoussuspensions of titanium dioxide. Desalination, 219(1-3), 301-311.

[30] So, C.M.; Cheng, M.Y.; Yu, J.C.; and Wong, P.K. (2002). Degradation ofazo dye procion red MX-5B by photocatalytic oxidation. Chemosphere,46(6), 905-912.

[31] E.E. Bamuza-pemu, E.M.N. Chirwa, "Profile of Aromatic Intermediatesof Titanium Dioxide Mediated Degradation of Phenol," *Chem. Eng.Trans.* vol.35, pp. 1333–1338, 2013.

[32] J. Latimer, J. Zheng. The sources, transport, and fate of PAH in the marine environment P.E.T. Douben (Ed.), PAHs: an ecotoxicological perspective, John Wiley and Sons Ltd, New York (2003)

[33] Roy, R.K., 1990. A primer on the Taguchi method. Van Nostrand Reinhold, New York, USA, ISBN:13-9780442237295, pages: 247