International Conference on Systems, Science, Control, Communication, Engineering and Technology 2015 [ICSSCCET 2015]

ISBN	978-81-929866-1-6		**VOL**	01
Website	icssccet.org		**eMail**	icssccet@asdf.res.in
Received	10 - July - 2015		**Accepted**	31- July - 2015
Article ID	ICSSCCET044		**eAID**	ICSSCCET.2015.044

Treatment methods for the removal of phenol from water- A Review

R. Subha[1], O.A.Sridevi[2], D.Anitha[3], D.Sudha[4]
[1, 2, 3, 4] Assistant Professors, Department of Chemistry,
Karpagam Institute of Technology, Coimbatore

ABSTRACT: *In recent years, there has been an enormous amount of research and development in the area of removal of phenol by various physio-chemical methods due to their carcinogenic nature and pungent odour. The MOEF has set a maximum concentration level of 1 mg/L of phenol in industrial effluents for safe discharge into surface waters, the WHO recommends a permissible phenolic concentration of 0.001 mg/L in potable water. Recent findings suggested that advances in nanotechnology and nano structured materials have allowed the modification of existing adsorbents which increase the potential of these technologies. Among various methods, adsorption is effective method due to simplicity, less economic and easy design.*

Key words: Phenol, Physio-chemical methods, Adsorption

1. INTRODUCTION

Water pollution by organic chemicals is a major problem over decades. The removal of organic contaminants from ground water or separation of contaminants present in polluted water has become a major focus of research and policy debate [1]. The presence of harmful organic compound such as phenols and their derivatives in water supplies and from industrial effluents is an ever increasing problem for the global concern[2]. Total phenol concentration in the wastewater of a typical Indian refinery processing 5.0 million tonnes of crude per year is around 135 mg/L and the discharge rate of wastewaters varies from 125 to 250 m^3 with pH being in the range of 8.8-9.4[3]. The ministry of environment and forests (MOEF), Government of India and EPA, United states have listed phenol and phenolic compounds on the priority pollutants list [4]. The MOEF has set a maximum concentration level of 1 mg/L of phenol in industrial effluents for safe discharge into surface waters, the WHO recommends a permissible phenolic concentration of 0.001 mg/L in potable water [3,5]. The major sources containing phenols are the wastewaters from processing, manufacturing industries engaged in oil refining, coal tar processing, petrochemical production, coke oven by products, plastic industry, textile processing, leather processing, insecticides production, manufacture of dyes and dyeing, glass production, etc[6]. Removal of phenol from industrial effluents is an important and dynamic area of research as well as being an important challenge, because environmental laws and regulations governing safe discharge levels are becoming increasingly stringent [7]. Several technologies including advance oxidation processes like Fenton, photo fenton, ozone oxidation, sono photo fenton and photo catalytic oxidation[8], membrane filtration [9], biological treatment [10], photocatalytic degradation [11], nanofiltration and adsorption[12]. Over the last decades, advances in nanotechnology and nanostructured materials have allowed the modification of existing adsorbents which increase the potential of these technologies [13]. This paper aims to review and summarize the various physiochemical methods for the treatment of phenol from water. Recent research on nano composites for improving phenol removal in water by means of metal, non metal and ion doping is also highlighted in this review.

Cite this article as: R. Subha, O.A.Sridevi, D.Anitha, D.Sudha. "Treatment methods for the removal of phenol from water- A Review." *International Conference on Systems, Science, Control, Communication, Engineering and Technology (2015)*: 199-203. Print.

2. TREATMENT METHODS

The fate of phenols in the environment and their removal from aqueous media is complicated by their low solubility, ability to ionize, low vapor pressure and tendency to undergo oxidation and oxidative polymerization with humic acid and fulvic acid-type products. The recent awareness of the toxic organic substances in wastewaters has generated interest in establishing effective treatment technologies.

A. Membrane filtration

B.

(i) Reverse osmosis

Separation methods for phenols which involve membranes are energy saving and can operate at room temperature. The separation of organic solutes from aqueous solutions by reverse osmosis has attracted attention, because of its energy saving nature. Typical operating pressures are in the range 15–50 bar, depending on the application. Reverse osmosis rejects monovalent ions and organics of molecular weight greater than about 50 (membrane pore sizes are less than 2 nm). The most common application of reverse osmosis is desalination of brackish water and seawater [14]. The rejection data of phenol using a commercial thin film composite polyamide reverse osmosis membrane are analyzed with the help of the combined film theory–solution–diffusion (CFSD) model and the combined film theory- Spiegler-Kedem. Although both the models can represent the experimental data available, the combined film theory- Spiegler-Kedem model predicted the rejection more accurately (max error ± 3%) than combined film theory–solution–diffusion (max error ± 10 %) model in phenol-water system. The $R_{o,max}$ predicted from both models are different, but there was no experimental verification as to which is more accurate. This analysis may be used to characterize reverse osmosis and nano filtration membranes[14].

(ii) **Ultrafiltration**

Ultrafiltration is similar in principle to reverse osmosis, but the membranes have much larger pore sizes (typically 0.002–0.03 mm) and operate at lower pressures. Ultrafiltration membranes reject organic molecules of molecular weight above 800 and usually operate at pressures less than 5 bar. The effectiveness of Membrane Ultra Filtration in removing organic compounds from aqueous stream owes to the fact that surfactant micelles containing these contaminants are too large to pass through the pores of the ultra filter [15,16,17] . Zeng et al. developed a micellar enhanced ultrafiltration of phenol in synthetic wastewater using two polysulfone spiral membranes of 6- and 10-kDa molecular weight cut–off and cetylpyridinium chloride as cationic surfactant. Polysulfone membranes could adsorb free phenol so that the concentration of permeate phenol was lower than that of free phenol. It was found that the phenol concentration of the feed, the permeate and the retentate cannot meet the material balance. The retenate phenol concentration kept increasing, and then decreased slightly with the increase of the feed cetylpyridinium chloride concentration [18].

(iii) **Nanofiltration**

Nanofiltration uses a membrane with properties between those of reverse osmosis and ultrafiltration membranes; pore sizes are typically 1-100 nm. Nanofiltration membranes allow monovalent ions such as sodium or potassium to pass but reject a high proportion of divalent ions such as calcium and magnesium and organic molecules of molecular weight greater than 200. Operating pressures are typically about 5 bar. Nanofiltration may be effective for the removal of color and organic compounds. Bodalo et al. studied the removal of phenol from aqueous solutions by nanofiltration using three experimental conditions and different membranes (NF-97, NF-99 and DSS-HR98PP). Three experimental conditions were carried out with different operating pressures: 10, 15 and 20 x 10^5 N/m^2, feed flow was kept constant at 2.78 x 10^{-5} m^3/s, pH=8 and T= 25°C. For each pressure feed phenol concentration was varied between 50 and 200 x 10^{-3} x kg/m^3. The different percentages rejection obtained between the nanofiltration membranes with feed phenol concentration variation can be attributed to the molecular characteristic of organic compounds such as acidity, solubility, ability to hydrogen bonding, etc. For the membrane NF-99, maximum value of water flux was obtained at pH 7. For membranes NF-97 and DSS-HR98PP the pH variation did not have a clear effect on the rejection percentages and solvent flux obtained[19].

B. **Solvent extraction**

Solvent extraction is the most often used technique to recover phenols from various aqueous effluents[20]. In membrane solvent extraction (MSE), there are two main kinds of membranes used: porous and nonporous. The solute within the membrane is transported from one side to the other side by a driving force, such as chemical potential differences across the membrane. Among porous membranes, microfiltration membranes have widely been applied for MSE process. Microfiltration membranes have pore sizes in the range of 0.1 to 10 microns, and so offer relatively low mass transfer resistance. Yang et al. developed a phenol removal process for the coal gasification wastewater. Based on the theoretical study and experiments, methyl isobutyl ketone was selected as the extracting solvent for the treatment of the coal gasification wastewater containing 5000 mg/L phenols and 20,000 mg/L COD. The results of the trial plant showed that more than 93% of the phenol in the wastewater was recovered, which was a by-product with economic benefit[21].

C. Ion exchange process

Ion exchange is a unit process in which ions of a given species are displaced from an insoluble exchange material by ions of a different species in solution. Ion exchange processes can be operated in batch mode or continuous mode. In a batch mode process, the resin is stirred with the water to be treated in a reactor until the reaction is complete. The spent resin is removed by settling, regenerated and reused. In a continuous process, the exchange material is placed in a bed of a packed column and the water to be treated is passed through it. When the resin is exhausted, the column is back-washed to remove trapped ions and the ion exchange resin is regenerated.

Lu et al. explored the proton exchange between phenol and ammonia or ammines based on density functional theory to show intracomplex proton exchange mechanism. The phenol-ammonia (parent) system possesses a barrier height (34.6 kcal/mol) of proton exchange. The results showed that the phenol tends to exchange hydrogen with the amines, preferably the secondary amines and the steric effect was favorable for the proton exchange. Finally, the calculations showed that the phenols radical cation $-NH_3$ system represented a barrierless proton transfer and remarkably low barrier (5.2 kcal/mol) of proton exchange, which support the importance of proton transfer in the proton exchange[22].

D. Advanced oxidation process

Advanced oxidation process (AOP) can be broadly defined as aqueous phase oxidation methods based on the intermediacy of highly reactive species such as hydroxyl radicals in the mechanism leading to the destruction of the target pollutant. Over the past 30 years, research and development concerning AOPs had been immense particularly for two reasons, namely the diversity of technologies involved and the areas of potential application. Key AOPs include heterogeneous and homogenous photo catalysis based on near ultraviolet (UV) or solar visible irradiation, electrolysis, ozonation, the Fenton's reagent, ultra sound and wet air oxidation, while less conventional but evolving processes include ionizing radiation, microwaves, pulsed plasma and the ferrate reagent. Depending on the properties of the waste stream to be treated and the treatment objective itself, AOPs can be employed either alone or coupled with other physiochemical and biological processes.

Chairez et al. proposed a new technique- differential neural network to estimate decomposition dynamics of phenols, byproducts accumulation and decomposition, and final products accumulation. The effect of increase in pH on the decomposition dynamics of phenol and 4-CP. 2, 4- DCP was very significant. It reduced the total decomposition time by a factor of 10. The presence of the chloro species in the phenol molecules also reduced the degradation time in ozonation[23].

Catalytic wet air oxidation of phenol with pelletized catalyst Ru/ZrO_2-CeO_2 was performed in a continuous packed bubble column reactor. The fresh and used Ru/ ZrO_2-CeO_2 catalysts were compared and it showed that introduction of ZrO_2 into Ru/CeO_2 increased the mechanical strength, specific surface area and adsorption capacity of pelletized catalyst. In the experiment of wet air oxidation of phenol with Ru/ ZrO_2-CeO_2 for 100 h, phenol and TOC removal stabilized around 100 and 96%, respectively[24].

Zairuddin et al. studied the degradation of phenol over the synthesized photo catalyst under the UV radiation in a batch reactor. The optimum formulation of supported nano TiO_2/ZSM-5/silica gel which consists of mixture of nano TiO_2, zeolite-5 supported in silica gel using colloidal silica gel as binder was found to be in the ratio of 1:0.6:0.6:1. 90 % of the phenol was degraded due to high surface area , low electron hole pairs, recombination rate and high crystalline quality of the synthesized catalyst[2]. Nanometric size Zn-doped TiO_2 photocatalyst was obtained by the oil/ water microemulison method. The increased photocatalytic activity in zn-doped TiO_2 with optimal zinc amount (5%) leads to the generation of surface oxygen vacancies in doped material promoting a decrease in the hole electron charge and the formation of tetracordinated Ti on nanomateral particles[13].

The degradation of phenol in air–equilibrated aqueous media was investigated using coupled sonochemistry and Fenton's reagent for a variety of operating conditions. The enhancement in the phenol degradation was mainly due to the contribution of additional hydroxyl radicals generated by Fenton's reagent as Fe (II) reacted with H_2O_2 (formed on sonolysis) enabling further production of $OH^{\cdot}$. The decomposition rate of aqueous phenol using coupled ultrasound and Fenton's reagent was strongly dependent on the initial concentration of reactant, Fe (II) concentration as well as pH[25].

E. Adsorption

Adsorption arises as a result of the unsaturated and unbalanced molecular forces that are present on every solid surface. Thus, when a solid surface is brought into contact with a liquid, there is an interaction between the fields of forces of the surface and that of the liquid. The solid surface tends to satisfy these residual forces by attracting and retaining on its surface the molecules, atoms, or ions of the liquid. Subha and Namasivayam, examined the feasibility of zinc chloride activated nano porous coir pith carbon for the removal of phenol from aqueous solution. Langmuir adsorption capacity was found to be 92.59 mg g^{-1} which was higher when compared to coir pith carbon in the absence of $ZnCl_2$ activation. Tests with synthetic wastewater showed that per cent removal of phenol by $ZnCl_2$ activated carbon was lower compared to pure phenol solutions due to the presence of other impurities that competed for adsorption sites[26]. Massalha et al. investigated the composite hydrophilic polyurethane (HPU) foams, which were enriched with various additives including dry biomass, clay and powdered activated carbon(PAC). The phenol adsorption capacity of the non-enriched foams was very low (2-8-5-4 mg/g foam).The enrichment of the foams by immersing in PAC aqueous solution, the maximal adsorption capacity of the adherent PAC on the foam was about 65% lower in average compared to free PAC[27]. Parker et al. revealed that the materials exhibited high efficiency to remove phenols from aqueous media due to the high mesoporous nature. The adsorption process was described well by Langmuir and Freundlich isotherms. Regeneration of starbon was attempted using a range of P^H with phenol recovery of upto 40% achieved[28]. Mohanty et al. investigated the nuts of Terminalia Arjuna,an agricultural waste were used to prepare activated carbons by zinc chloride activation under four different activation atmospheres. The carbons showed surface area and microporous volumes of around 1260 m^2/g and 0.522 cm^3/g, respectively. The maximum removal of phenol was obtained at P^H 3.5, above 93% for adsorbent dose of 10 g/L and 100 g/L initial concentration[6].

3.CONCLUSIONS

Todate, adsorption as well as photocatalytic degradation are widely explored as highly efficient adsorbent/metal oxides for removal of phenol from water. They exhibit various advantages such as fast kinetics, high capacity and preferable sorption/degradation towards phenol in water. Neverthless, the application of nano metal oxides (NMO) as adsorbent can be used for removal of phenol but the NMOs tend to aggreagate into large size particles and their capacity loss seems inevitable. Fortunately, fabrication of new NMO's based composite adsorbents seem to be an effective approach to respond to all the above technical problems.

Acknowledgement

The authors are grateful to the Management, Principal and Head of department of Karpagam Institute of technology for their continuous support and providing us lab facilities to carry out the research work

References

[1] P.A.Mangruklar, S.P.Kamble, J.Meshram, S.S. Raylu, "Adsorption of phenol and o-chlorophenol by mesoporous MCM-41", J.Haz Mat, vol: 160, pp: 414-421, 2008
[2] N.F.Zairuddin, A.Z.Abdullah, A.R.Mohamed, "Characteristic of supported nano TiO2/ZsM-5/Silica gel (SNT-2s) photocatalytic degradation of phenol, J Haz Mat, vol:174, pp:299-306, 2010.
[3]S.Mukherjee, S.Kumar, A.K. Misra, M.Fan, "Removal of phenol from water environment by activated carbon, bagasse ash and wood charcoal ", Chem Eng J, vol: 129, pp:133-142, 2007.
[4]M.Ahmaruzzaman, " Role of fly ash in the removal of organic pollutants from wastewater", Energy & fuels, vol: 23, pp: 1494-1511, 2009.
[5] WHO. Guidelines for drinking water quality, Third edition incorporating the 1st and 2nd addenda, Geneva, WHO Press, World Health Organisation, Switzerland, 2008.
[6] K. Mohanty, M.Jha, B.C.Meikap, M.N.Biswas, " Preparation and characterization of activated carbons from Terminalia Arjuna Nut with zinc chloride activation for the removal of phenol from wastewater, Ind Eng Chem Res, vol:44, pp:4128-4138, 2005.
[7] A.Hasanoglu, " Removal of phenol from wastewaters using membrane contactors: Comparative experimental analysis of emulsion pertraction", Desalination, vol: 309, pp:171-180, 2013.
[8] S.Bae,D.Kim,W.Lee, "Degardation of diclofenac by pyrite catalysed Fenton oxidation",Appl.Catal.B.Envion. , vol: 134-135, pp:93-102, 2013.
[9]K.Rzeszutek,A.Chow, " Extraction of phenol using polyurethane membrane",Talanta, , vol: 46, pp:507-519, 1998.
[10] A.P.Annachhatre,S.H.Gheewala, " Biodegradartion of chlorinated phenolic compounds", Biotechnol.Adv. , vol: 14, pp:35-36, 1996.
[11] A.Ahiileos,E.Hapeshi,N.P.Xekoukoulotakis,D.Mantzavinos,D.Fatta-Kassinos, "Factors affecting dichlofenac decomposition n water by UV-Tio2 photocatalysis"Chem.Eng.J, vol: 161, pp:53-59, 2010.
[12]T.X.Bui,S.Y.Kang,S.H.Lee,H.Choi, "Organically functionalized mesoporous SBA-15 as sorbents for removal of selected pharamecuticals from water",J.Hazard.Mater, , vol: 193, pp:156-163, 2011.
[13]M.S.D.G.Maria, C.Rodriguez, A.I.Arturo, V.Rodriguez, S.A. Vela-gonzalez, " Synthesis of Zn doped TiO_2 nano particles by the novel oil in water microemulsion method and their uses for the photolytic degradation of phenol", J.Env Chem Eng, in press , 2015.
[14]Z.V.P. Murthy, S.K Gupta, "Thin film composite polyamide membrane parameters estimation for phenol-water system by reverse osmosis", Sep Sci Technol, vol:33, pp:2541-2557,1998.
[15]B.R. Fillipi,J.F. Scamehorn and S.DChristian and R.W.Taylor , " A comparative economic analysis of copper removal from water by ligand-modified micellar-enhanced ultrafiltration and by conventional solvent extraction J Membr Sci, , vol:145,pp: 27-44,1998.
[16]L.L.Gibbs, J.F.Scamehorn , and S.D.Christian, "Removal of n-alcohols from aqueous streams using micellar enhanced ultrafilltration", J.Membr.Sci, vol:30, pp:67-74,1987.
[17]H.Adamczak,K. Materna, R.Urbanski, H.Szymanowski, " Ultrafiltration of micellar solution containing phenols", J.Coll.Interf.Sci, vol:218, pp:359-368,1999.
[18]G.M. Zheng, K.Xu, J.H.Huang, L.Xue, Y.Y.Fang, Y.H.Qu, " Micellar enhanced ultrafiltration of phenol in synthetic wastewater using polysulfone spiral membrane", J.Mem.Sci, vol:310, pp:149 – 160,2008.
[19] A.Bodalo, E.Gomez, A.M.Hidalgo, M. Gomez, M.D. Murcia, I. Lopez," Nanofiltration membranes to reduce phenol oncentration in wastewater". Desalination, vol:245, pp: 680-686,2009.
[20] M.Bielska,K.Materna,J. Szymanowski, "Cross-flow ultrafiltration of micellar solutions containing selected phenols" J. Env. Sci, vol:12, pp.233-258,2003.

Cite this article as: R. Subha, O.A.Sridevi, D.Anitha, D.Sudha. "Treatment methods for the removal of phenol from water- A Review." *International Conference on Systems, Science, Control, Communication, Engineering and Technology (2015)*: 199-203. Print.

[21] C.Yang, Y.Qian,L. Zhang,J.Feng, “Solvent extraction process development and on- site trial plant for phenol removal from industrial coal-gasification wastewater”Chem.Eng.J, vol:117,pp: 179-185,2006.

[22] Y.X.Lu, J.W.Zou,Z.M. Jin, Y.H.Wang,H.X. Zhang,Y.J. Jiang,Q.S. YU,” Proton exchangers between phenols and ammonia or amines: A computational study” J. Phys. Chem. A, vol:110, pp:9261-9266,2006.

[23] J.Chairez , A.Poznyak, T.Poznyak ,” Reconstruction of dynamics of aqueous phenols and their products formation in ozonation using differential neural network observers”, Ind. Eng. Chem .Res,vol: 46, pp: 5855-5866,2007.

[24] H.Wang,F. Zhao,S.I. Fujita, M.Arai, “Hydrogenation of phenol in $SCCO_2$ over carbon nanofiber supported Rh catalyst”, Cat. comm, vl:9,pp: 362- 368,2008.

[25] Y.Jiang, T.D. Waite, “ Degradation of trace contaminants using coupled sonochemistry and Fenton’s reagent” Water Sci Technol,vol: 47,pp: 85-92,2003.

[26] R.Subha and C.Namasivayam, “Kinetics and isotherm studies for the adsorption of phenol using low cost micro porous $ZnCl_2$ activated coir pith carbon”, *Can J Civ Eng* (NRC Research Press, Canada),vol: 8, pp:1-12,2009.

[27] N.Massalha, A.Brenner, C.Sheindorf, Y.Haimov, I.Sabbah, “Enriching composite hydrophilic polyurethane foams with PAC to enhance adsorption of phenol from aqueous solution, Chem Eng J, vol:280, pp:283-292, 2015.

[28] H.Parker, V.L.Budarin, J.H.Clark, A.J.Hunt, “ Use of starbon for the adsorption and desorption of phenol”, Sus Chem Eng J, vol:1,pp:1311-1318, 2013.

Cite this article as: R. Subha, O.A.Sridevi, D.Anitha, D.Sudha. “Treatment methods for the removal of phenol from water- A Review.” *International Conference on Systems, Science, Control, Communication, Engineering and Technology (2015)*: 199-203. Print.