International Conference on Systems, Science, Control, Communication, Engineering and Technology 2016 [ICSSCCET 2016]

ISBN	978-81-929866-6-1
Website	icssccet.org
Received	25 – February – 2016
Article ID	ICSSCCET152

VOL	02
eMail	icssccet@asdf.res.in
Accepted	10 - March – 2016
eAID	ICSSCCET.2016.152

Recent Methods for the Uptake of Chlorophenols from Nano Partciles-Review

R Subha[1], **D Subha**[2]

[1,2]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 uptake of chlorophenol by various physio-chemical methods due to their carcinogenic nature and pungent odour. The MOEF has set a maximum concentration level of 0.1 mg/L of chlorophenol 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.*

Keywords: *chlorophenol, Physio-chemical methods, Adsorption*

1. INTRODUCTION

Chlorophenols are a special group of chemicals that have attracted worldwide public attention, mainly due to their environmental persistence and their inherent toxicity to a broad spectrum of organisms. Monochlorophenols can be formed during wastewater chlorination, and as result of breakdown of pesticides and chlorinated aromatic compounds and their solubility in water is relatively high, CPs can easily migrate within different aqueous environments and contaminate ground waters [1]. Chlorophenols are an important class of xenobiotics that have been extensively used in the production of pesticides, herbicides and wood preservatives. They are listed as priority environmental pollutants by US EPA because of their higher toxicity, carcinogenicity and persistence [2].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 [3]. 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 [4]. 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 [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]. 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.

2. Treatment Methods

The fate of chlorophenols in the environment and their removal from aqueous media is complicated by their low solubility, ability to

Cite this article as: R Subha, D Sudha. "Recent Methods for the Uptake of Chlorophenols from Nano Partciles-Review". *International Conference on Systems, Science, Control, Communication, Engineering and Technology 2016*: 739-742. Print.

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.

(i) 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 bars. 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). 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 [14].

(ii). 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[15].

(iii). 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[16]. Saritha et al. (2009) reported a comparative assessment of 2,4,6-TCP degradation by advance oxidation process-UV,UV/H_2O_2, Fenton, UV/Fenton and UV/TiO_2 in the laboratory scale. Among all the processes, UV/Fenton process was found to be more efficient in degrading 2,4,6-TCP (90%) and the degradation rate with the UV/Fenton process was almost ten times higher than UV alone, as evidenced by kinetic constant values. The optimum conditions obtained for the best degradation with UV/Fenton were: pH=3, Fe^{2+} concentration of about 5 mg/L and peroxide concentration of 100 mg/L for an initial 100 mg/L of 2,4,6-TCP concentration. The efficiency of dechlorination was found to be dependent on substituents present on the aromatic ring and the photo-fenton process showed a greater tendency to liberate Cl^- ions (about 88%) than the other processes [17].

(iv) a. Ozonation

Ozone is a strong oxidant that either decomposes in water to form hydroxyl radical which are stronger oxidizing agents than ozone itself thus inducing the so-called indirect oxidation or attacks selectively certain functional groups of organic molecules through an elctrophillic mechanism [18,19]. Depending on the type of the substrate and the operating conditions, ozone oxidation is usually favored at higher pH values due to the increased production of hydroxyl radicals. Ozonation has been traditionally employed in drinking water

Cite this article as: R Subha, D Sudha. "Recent Methods for the Uptake of Chlorophenols from Nano Partciles-Review". *International Conference on Systems, Science, Control, Communication, Engineering and Technology 2016*: 739-742. Print.

treatment for odor and taste control and disinfection, as well as for wastewater disinfection [20]. Ozonation at high pH (>8) is also regarded as a AOP because decomposition of ozone molecule into hydroxyl radicals is predominant under such conditions and the reactions between the radicals and organic molecules take place [21]. Chairez et al. (2007) proposed a new technique- differential neural network to estimate decomposition dynamics of phenols, byproducts accumulation and decomposition, and final products accumulation. The technique has been tested to compare estimated results to those experimentally obtained during semibatch ozonation of the model solution of phenols. 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.

Oxidation of substituted phenols, chlorophenols and nitrophenols at atmospheric pressure by ozone over a copper-alumina catalyst was studied. The degradation of phenols increased with the ozone dose (3.5 mg/min).The increase of initial pH value caused a major increase of the phenol conversion for the unanalyzed process (71 %) and a more temperate one for the catalyzed process (74.9%). The efficiency of the catalytic process was improved by raising catalyst concentration up to 2 g/L. The reactivity of the substituted phenols (4-CP>2-CP>4-NP>>2-NP) was found both in the catalyzed and uncatalyzed processes, but the difference between their conversion values was low in the presence of the catalyst [22].

Anotai et al. (2007) investigated that PCP degradation and detoxification by ozone and found that the degradation rate of PCP was controlled by the mass transfer rate of ozone from gas to liquid phase. The detected intermediates were 2,3,4,6- and 2,3,5,6-TeCPs, and phenol. The toxicity of PCP and TeCPs were found to be comparable but they were less toxic than their less chlorinated congeners and phenol [23]. Pandiyan et al. (2006) studied the photooxidation of chlorophenols and compared with electrochemical methods. It has been found that 4-CP was oxidized faster than other chlorinated phenols because higher chlorinated phenols were hard to decompose. The order of decomposition was 4-CP>2,4-DCP>2,4,6-TCP>PCP in both the electrochemical and photochemical methods. Factors such as the columbic repulsion between the elctrophile, $OH^{\cdot}$ radical and electron-deficient PCP ring was mainly affecting the degradation of PCP. Despite several advantages of using ozone, it has a few disadvantages, which limit its application in water treatment technology due to relatively low solubility and stability in water. Because of the high cost of ozone production and partial oxidation of organic compounds present in water, the application of ozonation might not be feasible from an economic point of view [25].

(v) Photocatalysis

The photo catalytic oxidation (PO) of the organics in wastewater can be made more efficient by careful selection of the catalyst combined with UV. The UV activates the catalyst, which results in the formation of reactive radicals. Ochuma et al.(2007) reported that the pilot scale concurrent down flow contactor reactor equipped with a 1.0 or 2.0 kW lamp was capable of total degradation and mineralization of 2,4,6-TCP. Under optimized reaction conditions, 100 % conversion of 2,4,6-TCP was achieved in 180 min using 15 ml solutions with initial concentration of 120 mg/L. Using the 1 kW or 2 kW UV lamps, conversion of 100 mg/L of 2,4,6-TCP after 30 min was 62.51 % and 90.71 % , respectively, with initial reaction rate of 1.33×10^{-5} and 4.22×10^{-5} mol/min, respectively and the rate constant 0.0046 x 0.29/min, respectively.

Gao et al. (2007) reported that TiO_2 nanotubes was prepared and characterized, and inferred from EPR signal that the active oxygen species $OH^{\cdot}$ are generated by TN-400. The degradation of PCP was faster by microwave assisted photocatalysis than photolytic alone or microwave alone or dark process. PCP was efficiently degraded in the microwave assisted photo catalysis process on TN-400. The removal of 40 mg/L of PCP was 93.5 %, the COD_{cr} removal efficiency was 51.8 % in 20 min, pH decreased from 10.3 to 7.5 and the process of dechlorination was completed in 12 min.

(vi). Wet Air Oxidation

Wet air oxidation (WAO) and CWAO use temperature and pressure over $120^{\circ}C$ and 10 bar and air or oxygen as oxidant. It was particularly useful for toxic organic wastewater [28]. Depending on the reaction conditions two objectives could be achieved: a) complete mineralization of organics to CO_2 and H_2O or b) only an increase of the effluent biodegradability by adjusting the conversion of toxic organic matter to the formation of biodegradable by-products such as carboxylic acids (Oliviero et al., 2003). Chalilha and Bhattacharya (2008) used Fe (III), Co(II) and Ni(II) incorporated MCM41 mesoporous solids for oxidation of 2,4,6-TCP in water with or without the oxidant, H_2O_2. The conversion achieved with Fe(III), Co(II) and Ni (II) incorporated MCM41 in 5 h was 59.4, 50.0, and 65.6 %, respectively, with 2,4,6-TCP: H_2O_2 molar ratio of 1:1, and 60.2, 60.9 and 68.8 % in the absence of H_2O_2. Higher percentage of conversion was achieved when the pH was near 7.0 and the natural pH of 2, 4, 6-TCP aqueous solution (5.5) was sufficient to bring about considerable destruction.

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

Cite this article as: R Subha, D Sudha. "Recent Methods for the Uptake of Chlorophenols from Nano Partciles-Review". *International Conference on Systems, Science, Control, Communication, Engineering and Technology 2016*: 739-742. Print.

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.

References

1. Armenante, P.M., Kafkwitz, D., Lewandowski, A., Jou, C. J., 1999. Anaerobic –aerobic treatment of halogenated phenolic compounds. *Water Res*, 33, 681-692.
2. Agency for toxic substances and Disease Registry (ATSDR), (2001).Toxicological profile for PCP
3. 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
4. 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.
5. S.Mukherjee, S.Kumar, A.K. Misra, M.Fan, Chem Eng J, vol: 129, pp:133-142, 2007.
6. Ahmaruzzaman, "Role of fly ash in the removal of organic pollutants from wastewater", Energy & fuels, vol: 23, pp: 1494-1511, 2009.
7. WHO. Guidelines for drinking water quality, Third edition incorporating the 1st and 2nd addenda, Geneva, WHO Press, World Health Organisation, Switzerland, 2008.
8. 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.
9. A.Hasanoglu, "Removal of phenol from wastewaters using membrane contactors: Comparative experimental analysis of emulsion pertraction", Desalination, vol: 309, pp: 171-180, 2013.
10. 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.
11. K.Rzeszutek,A.Chow, " Extraction of phenol using polyurethane membrane",Talanta, , vol: 46, pp:507-519, 1998.
12. A.P.Annachhatre, S.H.Gheewala, "Biodegradartion of chlorinated phenolic compounds", Biotechnol. Adv. vol: 14, pp: 35-36, 1996.
13. 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.
14. 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.
15. 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.
16. 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
17. Saritha, P., Samuel Suman Raj, D., Aparna, C., Vijay Laxmi, P.N., Himabinu, V., Anjaneyulu,Y.," Degradative oxidation of 2,4,6-trichlorophenol using an advanced oxidation process- A Comparative study". Water Air Soil Poll, 200, 169-179, 2009.
18. D.Mantzavinos, E. Psillakis, "Enhancement of biodegradatibility of industrial wastewaters by chemical oxidation pre-treatment". J Chem Tech Biotechnol, 79, 2007 431-454.
19. Dantas, R.F., Canterino, M., Marotta, R., Sans, C., Esplugas, S., Andreozzi, R., "Bezafibrate removal by means of ozonation: primary intermediates, kinetics, and toxicity assessment". Water Res, 41, 2525-2532, 2007.
20. Klavarioti, M., Mantzavinos, D., Kassinos, D., "Removal of residual pharmaceuticals from aqueous system by advanced oxidation process". Env Int, 35, 402-417, 2009.
21. Ikehata, K., Gamel El-Din, M., "Aqueous pesticide degradation by ozonation and ozone based advance oxidation processes: a review (Part II)". Ozone: Sci Eng, 27, 173-202, 2005.
22. Udrea, I., Bradu, C., "Ozonation of substituted phenols in aqueous solution over CuO-Al_2O_3 Catalyst". *Ozone Sci Eng,* 25, 335-343, 2003.
23. Anotai, J., Wuttipong, R., Visvanthan, C., "Oxidation and detoxification of pentachlorophenol in aqueous phase by ozonation". *J Env Mang*, 85, 345-349, 2007.
24. Pandiyan, T., Martinez Carrillo, M.A., Matamoros Flores, H., Ruiz Santoyo, M.E., Duran De Bazua, C.," Photochmeical oxidation of chlorinated phenols in comparison with electrooxiadtion". Toxic Env Chem, 88, 23-33, 2009.
25. Ochuma, I.J., Fishwick, R.P., Wood, J., Mike Winterbottom, J.," Photocatalytic oxidation of 2,4,6-trichlorophenol in water using a concurrent down flow contactor reactor (CDCR)". J Haz Mat, 144, 627-633, 2007.
26. Bhargava, D.S., Sheldarkar, S.B., "Use of TNSAC in phosphate adsorption studies and relationships. Effects of adsorption operating variables and related relationships". Water Res*,* 27, 303-312, 1993.

Cite this article as: R Subha, D Sudha. "Recent Methods for the Uptake of Chlorophenols from Nano Partciles-Review". *International Conference on Systems, Science, Control, Communication, Engineering and Technology 2016*: 739-742. Print.