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# Optimization of Photocatalytic Degradation Parameters of Parachlorophenol by UV/ZnO system: Identification of Intermediates Using Ultra Performance Liquid Chromatography Coupled with High Resolution Orbitrap Mass Spectrometry

DIPALI KALE AND PRAGATI THAKUR[+]

The photocatalytic degradation and mineralization of 4-Chorlophenol (4-CP) in aqueous solution was examined under UV/ZnO system. The characterization of ZnO was performed using scanning electron microscopy and diffuse reflectance spectroscopy. The influence of substrate concentration, catalyst dose and pH on photodegradation was studied. Under optimized conditions ([4-CP]= 50 mg $L^{-1}$, [ZnO] = 2 g $L^{-1}$ and pH = 7), % removal of total organic carbon (TOC) and chemical oxidation demand (COD) values were 73 and 50, respectively within 60 min and the complete mineralization was achieved in 2 hours. The degraded intermediates of 4-CP were identified using high resolution mass spectrometry and FTIR spectroscopy. The use of high resolution mass spectrometry has allowed accurate identification (mass accuracy < 10 ppm) of four known and two unknown intermediates. This data supports hydroquninone and 4-chlorocatechol pathways of 4-CP degradation. The present work demonstrates the use of heterogeneous photocatalysis for successful removal of organic contaminants such as chlorinated phenols.

**Key words**: *Photocatalysis, 4-Chlorophenol, Zinc Oxide, Intermediates, high resolution liquid chromatography-mass spectrometry*

## Introduction

Due to rapid industrialization, urbanization and agricultural growth there is tremendous increase in the environmental pollution. In developing countries the water resources are becoming increasingly polluted due to the release of effluents without adequate treatment. Hence, EPA (Environmental Protection Agency) has enforced stringent laws and regulations to control effluent quality parameters such as chemical oxygen demand (COD), biological oxygen demand, total dissolved solids and total organic carbon (TOC) values within permissible limits.

Chlorinated phenols constitute a major class of toxic and hazardous water pollutants as their exposure leads to various harmful immunological, neurological, reproductive, genotoxic and carcinogenic health effects. They are included in the United States EPA [1] and European Union [2] priority pollutant list with an upper permissible limit of 0.5 mg $L^{-1}$ in potable water [3]. 4-chlorophenol (4-CP) is one of the most toxic and ecologically persistent environmental pollutants with challenges in its biodegradation [4]. Apart from commercial synthesis, 4-CP is also produced from bleaching of pulp [5], chlorination of phenol-containing drinking water [6] and as an intermediate in the degradation of chlorophenoxy herbicides [7]. Hence, there is a need of cost effective, simple and environment-friendly degradation methodology for its safe disposal. Accordingly, substantial efforts have been dedicated in developing purification methods to destroy this bio-recalcitrant aqueous phenolic compound. Incomplete removal of 4-CP during treatment processes has raised public and regulatory concern due to its genotoxicity and carcinogeneticity. Furthermore, the usual techniques generate waste and require additional steps with incurred cost [8].

Advance oxidation processes such as semiconductor mediated photocatalysis have been established for the degradation and mineralization of gaseous [9, 10] and aqueous phase pollutants [11-13]. $TiO_2$ has been traditionally used for the photocatalytic degradation of various pollutants owing to its non-toxicity, high photoactivity and photostability. ZnO has been considered as a suitable alternative for $TiO_2$ due to its similarity with $TiO_2$ band gap (ZnO; 3.4 eV and TiO2; 3.2 eV), photodegradation mechanism[14] and its relative inexpensiveness. The greatest advantage of ZnO over $TiO_2$ is its broader absorption spectrum in comparison with $TiO_2$ [15]. Purification of water by ZnO photocatalysis results in high reaction and mineralization rates due to efficient generation of $H_2O_2$ [16]. Further the superior performance of ZnO compared to $TiO_2$ is reported in case of photodegradation of several pollutants [17-19].

The present study investigated the photocatalytic degradation of aqueous solution of 4-CP by ZnO particles

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J. Environ. Science & Engg. Vol. 58, No. 3 p. 185-192, July 2016

# GIS Based DRASTIC Model for Assessment of Groundwater Vulnerability in Puri City, India

RITESH VIJAY[1+], S. S. RAMYA[1] AND P. K. MOHAPATRA[2]

Groundwater pollution is mainly caused due to the domestic and industrial activities which pollute the shallow aquifers. Puri city is such an important and pilgrim place where groundwater is getting contaminated by various anthropogenic activities. The vulnerability assessment of groundwater is mainly carried out to define the areas critical for the groundwater contamination. For this, GIS based DRASTIC model was used to assess the groundwater vulnerability considering groundwater level, hydro-geological parameters, land use pattern and topographic condition. It was found that most of the city area is highly vulnerable to groundwater contamination due to sandy aquifer property. The output of DRASTIC model helps in suggesting measures for protecting the groundwater from further contamination and management.

**Key words:** *DRASTIC, aquifer, GIS, vulnerability, groundwater quality*

## Introduction

The quality and quantity of groundwater are both equally important because groundwater is the only source of drinking water in most of the urban areas of India[1]. Due to high growth of population, unplanned growth of cities, mixed land-use patterns, lack of proper sewage system and poor disposal of wastewater both from domestic and industrial activities are deteriorating the groundwater quality in several Indian cities in recent years[2]. The assumption in the assessment of groundwater vulnerability is that the geological environment ensures a sufficient degree of protection against the anthropogenic impact. Almost 70% of the surface water resources and most of the groundwater reserves are already contaminated by biological, organic and inorganic pollutants[3]. The vulnerability of groundwater to pollution can be articulated as the sensitivity of its quality to anthropogenic activities for assessing their effects upon groundwater[4].

The accuracy of aquifer vulnerability assessment depends on the availability of complete and reliable hydrodynamic and hydro-chemical information, data on the location of potential pollution sources and the type and physico-chemical properties of pollutants[5,6]. A number of models are available for assessing the aquifer vulnerability to contamination. Among these models, the most comprehensive and frequently used model in assessing groundwater vulnerability is the DRASTIC model[7]. Further, Geographical Information System (GIS) technique has provided an efficient tool for assessing and analyzing the vulnerability to groundwater pollution[8]. Therefore, the aim of the present study was to develop a GIS based DRASTIC model for the assessment of aquifer vulnerability to groundwater contamination in Puri city.

## Study area

Puri city is situated on the shoreline of Bay of Bengal and lies between 19° 472 and 19° 502 N latitudes and 85° 482 and 85° 522 E longitudes (Fig 1). The city area is around 16.84km$^2$. The climate of Puri is warm-humid with the maximum and minimum temperature 37.5°C and 27°C in the summer while 28.2°C and 15.2°C in winter, respectively[9]. River water is not sufficient and suitable for water supply due to non-perennial nature and salinity due to backwater of sea. Therefore, the city receives water supply of about 20.44 million liters per day (mld) from groundwater resources namely Chakratirtha water field (CTWF) on the eastern side and Balia Panda water field (BWF) on the western side of the city[11].

The major hydrogeological units occurring in this area are unconsolidated and porous formations. The sand gravel layers are the main repositories of groundwater in the area. The groundwater at shallow depths occurs under phreatic conditions, and thickness of individual aquifers varies from 6 to 79m[12]. There is a high water table fluctuation in the Puri city. The depth of water table is very less in the post-monsoon season which indicates that those areas are very high vulnerable to contamination[13]. The groundwater quality of Puri city was deteriorated due to the discharge of effluent from septic tanks; soak pits, pit latrines, discharges of domestic wastewater in leaky drains, and leachate from solid waste dumpsite[14]. The groundwater is getting contaminated in city area as compared to Chakratirtha and Balia Panda water fields

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J. Environ. Science & Engg. Vol. 58, No. 3 p. 193-198, July 2016

# Bird Diversity in Relation of Water Quality in Patela Pond and Surrounding Wetland

POOJA DUBEY[1], LALIT CHAUDHARY[2], AND SEEMA BHARADWAJ[3*]

Patela pond is situated near Talwara village 12kms away from of the Banswara city. This pond is located at Longitude of E074º-19'20.31" and Latitude of N-23º-33'43.13". Annual rainfall of this area is about 856mm and flooding months are July and August. Some part of this pond is covered by different kinds of aquatic weeds. Solid waste was dumped on a part of the bank of this pond. Few agricultural fields are present nearby this pond. A wetland area is also found near this pond. 52 species of birds belong to 24 families and 9 orders were noticed in Patela pond and its near wetland area. Level of nutrient content and food availability of this area and physicochemical conditions of the study site are in favor of the maintenance of bird diversity. The Relative Diversity index (RDi) of different families of birds were ranged from 1.92 to 26.88 in different seasons. Anatidae was the most dominating family in this area with the highest number of bird species. The relative diversity index of this family was also highest (RDi = 26.88). The water temperature was ranged between 16.70! to 39.00!, the value of D.O. exhibited marked variation during different months from 4.25ppm to 6.80ppm, pH of water varied between 7.60 to 8.20. The water of the study site has shown fluctuations in the value of depth of visibility, alkalinity, nitrate, and phosphate. Value ranged from 37.00cms to 57.00cms, 138.75 to 162.80 and 0.80 to 1.20, 0.70 to 1.10 for the depth of visibility, alkalinity, nitrate, and phosphate respectively. This study would be useful for future initiatives related with the bird's status, bird diversity, bird's conservation, pollution status and planning of ecotourism.

**Keywords :** *Patela, Bird diversity, Wetland, Physicochemical parameters.*

## Introduction

Birds also act as zoo indicators of water quality. The long existence of aquatic bird populations in typical conditions can act as a model for the study of the response of that bird population in that water quality. Water quality affects birds during the nesting period. In this period many reproductive parameters such as stability of bird groups, fecundity, nesting, proper nest formation, egg size, egg number and incubation period [1]. Bird's habitats included wetlands, ponds, lakes, dams, reservoirs, rivers, streams, agricultural fields, and forests, etc. Wetlands are important areas for wildlife protection, recreation and flood prevention [2]. Wetlands are the cradle of bird diversity. These habitats are transitional between aquatic and terrestrial ecosystems. The importance of the study of wetlands is increasing day by day because they provide good habitats for aquatic life and water availability for surrounding fauna and flora. Wetlands are very productive aquatic ecosystems and they provide an excellent habitat platform to aquatic biodiversity [3].

Wetlands are the world's very productive ecosystems therefore they have characterized by the rich diversity of birds [4][5]. Wetlands usually regulate water quality, micro habitat, macro habitat and unique habitats to fauna [6]. The physicochemical quality of habitats directly shows the influence on birds feeding, migration reproduction and other behaviors. Wetlands are intermediary sites between terrestrial and aquatic ecosystems. Studies of those sites are related to the monitoring of water quality and biodiversity [7]. The cover percentage of dominating vegetations such as Typhya species, B. fluviatilis, and P. arundinacea. They also estimated the percentage of open water areas for study-related with habitat [8]. Aim of this study was to deal with the relation of water quality and bird diversity in Patela pond and its wetland.

## MATERIAL AND METHODS

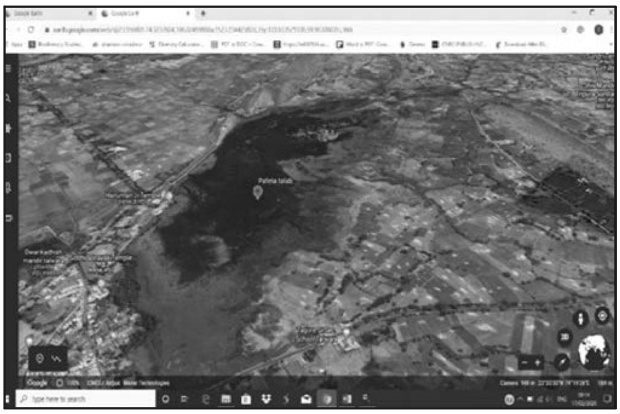

**Fig. 1 : Study area**

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# Macroinvertebrates Diversity in Relation with Physico-chemical Stability in Sahashradhara Springs of Doon Valley, India : A First Report

RAMESH C. SHARMA[1], ANITA CHAUHAN[1+] AND NEETU SINGH[1]

The Sahashradhara, a group of one thousand springs, is one of the most important clusters of limnocrenes and rheocrenes types of springs located in Doon Valley of the Garhwal-Himalayas. A maiden attempt has been made to present on the biodiversity of macro-invertebrates and physicochemical stability on the Sahashradhara springs. A minor monthly variation in the physico-chemical parameters in comparison to other water bodies or water courses-rivers, streams and lakes of Garhwal Himalayas has been recorded in the Sahashradhara springs, showing physico-chemical stability. Nymphs and larvae of Ephemeroptera, Plecoptera, Trichoptera, Diptera, Coleoptera and few members of Annelida and Mollusca represented the macroinvertebrates dwelling the Sahashradhara springs. Annual percentage composition of macroinvertebrates contributed by various taxa revealed that major contribution was made by Ephemeroptera (36-48%) followed by Plecoptera (13-17%), Diptera (9-14%) and Tricoptera (8-13%). A total of 39 species of macroinvertebrates were recorded from different springs of Sahashradhara. A significant correlation between temperature, turbidity, conductivity, dissolved oxygen, free $CO_2$, alkalinity, FPOM and CPOM and density and diversity macroinvertebrates was observed. Result of regression analysis performed between the density of macroinvertebrates and physico-chemical variables revealed that the temperature, conductivity, alkalinity, $CO_2$, TDS, CPOM and FPOM were found to strongly influence the density and diversity of macroinvertebrates of Sahashradhara springs. Diversity of macroinvertebrates was found to have a negative correlation with water temperature ($r= - 0.88; p<0.001$), CPOM ($r= - 0.85; p<0.001$) and FPOM ($r= - 0.77; p<0.01$) respectively; whereas diversity of macroinvertebrates was found to have positive correlation with dissolved oxygen ($r= 0.70; p<0.01$) and alkalinity ($r= 0.81; p<0.001$), respectively.

**Key words**: *Sahashradhara, Doon Valley, Garhwal Himalayas, limnocrenes, rheocrenes, ephemeroptera, plecoptera, trichoptera*

## Introduction

Springs are considered to be ‘hotspots’ for aquatic biodiversity due to stability in their physico-chemical characteristics (Williams and Williams 1998, Cantonati *et al.* 2006)[43,11]. Springs have high ecological value in spite of their usually small sizes (Odum 1971)[25]. Springs are ecotones linking an aquifer to the upper most section of a surface running water system. The unique characteristics of springs are that these habitats are three-way ecotone where groundwater, surface water and terrestrial ecosystem interact. Thus, springs are interface between several distinct ecosystems creating a heterogenous mosaic of aquatic, semi aquatic and semi terrestrial microhabitats.

Spring systems have great faunistic and biogeographic value; despite their importance, their biology and ecology have become a topic of intensive investigation only recently. The macroinvertebrate composition of springs are affected by change in environmental, physical and chemical factors like water chemistry (Glazier 1991)[15], water current velocity (Ilmonen and Paasivirta 2005)[17], substratum composition (Glazier and Gooch 1987)[14] or altitude (Barquín and Death 2006)[4]. Several research studies on biodiversity of springs have been conducted at the international level (Williams 1991; Roca and Baltanes 1993; Botosaneaenu 1998; Williams and Williams 1998; Mezquita *et al.* 1998; Stoch 2001; Natheson *et al.* 2003; Rosetti *et al.* 2005; Cantonati *et al.* 2006; Pieri *et al.* 2007; Brown and Hannah 2008; Sander *et al.* 2010; Maiolini *et al.* 2011; Spitale *et al.* 2012; Feldar and Fumetti 2013; Rosati *et al.* 2014)[44,30,8,43,38,24,32,11,9,34,22,36,12,31].

However, a few scattered reports on some geological and limnological aspects of the springs of the Himalayas in India are available. Unfortunately, no work has been done so far on the study of macroinvertebrate diversity and physico-chemical stability of springs of Garhwal Himalayas. Therefore, the present study on the biodiversity of springs and their physico-chemical stability in Doon Valley, Garhwal Himalayas has been done. To the best of our knowledge, this will be the

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# Enhanced Primary Treatment of Sewage by Sand and Alum Sludge Ballasted Flocculation

G. R. MUNAVALLI*+ AND V. B. GURAV**

An experimental work was conducted to study feasibility of using ballasting agents for the removal of organic matter and suspended solids from sewage. A series of jar tests were carried out on sewage using clean sand, re-injected sand and alum sludge as ballasting agents. The use of polymer is essential for effective application of ballasting agents. Alum aided sludge ballasted flocculation was found to be more effective than that with only alum sludge. Sand, re-injected sand, and alum-sludge ballasted flocculation contributed 10 % to 15 % more for removal of COD and turbidity than that of conventional coagulation. Efficiency of ballasted flocculation with lower coagulant dose and lesser settling time is more than that of conventional coagulation with relatively higher coagulant dose and higher settling time. Grit (sand) from sewage treatment plant can be used as a ballasting agent.

**Key words:** *Ballasted flocculation, coagulation, sewage, jar test, organic matter, polymer, sand, turbidity*

## Introduction

Sewage is composed of organic and inorganic matter in the form of suspended, colloidal, and dissolved solids. In a typical primary treatment, the removal efficiency of Suspended Solids (SS) and Chemical Oxygen Demand (COD) is around 50% and 30%, respectively. The lower efficiency is attributed to partial removal of finely divided suspended particles that account for a large portion of the SS. The removal of small particles (< 50 μm) is almost impossible in a conventional primary sedimentation tank1. Chemically Enhanced Primary Treatment (CEPT) involves addition of chemical coagulant and flocculent aid to the wastewater. CEPT is effective to remove finer particles and further reduces organic load on secondary treatment. The large amount of floc developed in CEPT needs to be rapidly settled out by providing more surface area for the attachment of microfloc. Sand and dense-sludge ballasted flocculation processes are the potential options for enhanced settling, higher rate of clarification and heavy floc formation.

Ballasted flocculation is a process in which sand/dense-sludge and polymer are injected to ensure the formation of dense and homogeneous floc particles thereby improving the settling properties of SS through improved floc bridging2. The objective of this process is to form microfloc particles with a higher specific gravity. Rapid floc formation and reduction in particle settling time induce high rate clarification thereby allowing treatment of flows at a significantly higher rate than allowed by conventional unit processes. ACTIFLO (US filter) and DensaDeg (Infilco Degremont technologies), used the concept of ballasted flocculation for various applications.

Sand Ballasted Flocculation (SBF) study on water treatment has been carried out at laboratory scale so as to assess its effectiveness for turbidity removal, to understand mechanism of ballasted floc formation and to know factors affecting ballasted flocculation reactions3-7. The treatment of wet weather flow/wastewater was studied using sand/sludge ballasted flocculation by8-13. A study was carried out on the feasibility of reusing water treatment works sludge (''alum sludge'') to improve particulate pollutant removal from sewage14. CaF2 sludge was used for improving the fluoride removal from industrial wastewater15.

It can be seen from literature cited above that sand and chemically conditioned dense-sludge have the potential to enhance suspended solids removal and rate of clarification. There are very few studies reported on enhancement of primary treatment of sewage using ballasted flocculation. The relative performance of various ballasting agents for treating the same quality of sewage has not been reported in the literature. The effect of repeated usage of sand (re-injected sand) as ballasting

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# The Emission Gap: Assessment of NDCs Pledges with Reference to G-20 and India

DR. MAHENDRA KUMAR MEENA

In the history of climate change regime, in year 2010 and 2015, countries submitted their self determined GHG emission reduction targets through NAMAs (Cancun, 2010) and NDCs (Paris 2015). It is pertinent to mention that the world unanimously accepted the threshold to temperature rise below 2°C or in best scenario 1.5°C by the year 2100. The important question arises here, weather these pledges would sufficient to save the temperature goal or we need to increase grave efforts with greater intensity? In the present paper, an attempt has been done to assess adequacy of mitigation pledges made by, specially the G-20 countries with additional emphasis on India.

**Keywords:** *Climate Change, Regime, GHG, Mitigation Pledges, Temperature rise, NDCs*

## INTRODUCTION

Since the adoption of the United Nation Framework Convention on Climate Change (UNFCCC) in 1992, the world has been gathering annually to decide the fate of the living earth. So far, two remarkable achievements can be recognized towards curbing the Green House Gases- responsible for the rise in average global temperature- one is Kyoto Protocol (1997) and Paris Agreement (2015). By the year 1990, the science of climate change and its repercussions had been well understood by the world under the auspices of the Inter Governmental Panel on Climate Change (IPCC). From 1992 to the Copenhagen Summit 2009, the political leaders of nations were largely engrossed in the grave business of deciding the responsibilities of mitigation actions, financing and the technological assistance. The Copenhagen summits was historical in context of changing the basic arguments, the Common but Differentiated Responsibility (CBDR) that had been embraced as the bedrock of future negotiations under the UNFCCC. Unlike the Kyoto Protocol, Copenhagen Summit adopted self determination approach to offer mitigation action plans. Now, the differentiation between developed and developing countries in context of mitigation actions was thinner or almost ended. Subsequently, countries offered their emission reduction pledges on volunteer basis in form of Nationally Appropriate Mitigation Actions (NAMAs) that had to be implemented by 2020.

In 2015, at Paris, the Conference of Party to the UNFCCC agreed to keep the average rise in global temperature above pre industrial level within $2^0$ C and in best scenario $1.5^0$C by 2100. As the Paris Agreement decided that each party would offer its Intended Nationally Determined Contribution (INDC), contained with their plan of actions and quantified GHG reduction targets. The Paris Agreement (Article 4, para2) requires each party to prepare, communicate and maintain successive nationally determined contributions (NDCs).[1] The submitted NDCs will be implemented from 2020 to stabilize the rise in temperature within $2^0$ C. The NDCs will have to be submitted on incremental basis in every 5 year.

## 1. The Concept of Emission Gap

The Copenhagen Accord associated around 140 countries and 85 countries had made pledges to reduce GHG emissions till the year 2020.[2] But, still, the critical question was on the board, weather the pledges would be sufficient to hold the rise in global temperature below $2^0$ C above pre industrial level? Or there would be any gap between required and offered pledges. To assess these pledges and their consistency with $2^0$C goal, the United Nations Environmental Programme (UNEP) in conjunction with the European Climate Foundation and the National Institute of Ecology, Mexico had carried out a six month study by compiling various studies.[3] This was the first "Emissions Gap Report" released in 2010. The UNEP has been releasing the Emission Gap Report on annual basis. The 10th edition of the report was released on 26 November 2019. The report is containing with alarming conclusions and warranting urgent mitigation action to narrow down the emission gap to curb repercussions of climate change.

For the purpose of definition, we can rely on the simple definition offered by the World Resources Institute (WRI) *"the difference between the emissions level countries have pledged to achieve under international agreements and the level consistent with limiting warming to well below 2 degrees C (3.6 degrees F).*[4] In other words it can be described as *"the difference between where we are likely to be by 2030 and where we need to be has become known as the 'emissions gap'*.[5] The difference can be measured from the pledges that had been made in 2010-2011 as NAMAs or more precisely from the pledges (NDCs) have been made in Paris Agreement. For this paper, pledges made in Paris Agreement by top emitters, have been taken to assess the emission gap in 2030.

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