Specifically, among others, this book discusses (i) need to evaluate mathematical modelling of wastewater treatment, allocation systems, supply, persistence of pollutants and filtration and nanotechnology, (ii) monitoring quality of water for environmental discharge, mining discharge, by benthic community and mechanisms of environmental interactions, (iii) understanding the procurement, ground water quality and quantity measuring techniques, pharmaceutical products in water, water quality index, water governance structure, effects of organic soil conditioners and organic fertilizers application (GHG and underground waters), impacts of the treatment methods such as chlorination, and use of readily available biomass as adsorbents of water pollutants. Finally, emerging approaches such as water treatments by photocatalytic methods, combinatorial/factorial approach, solid and liquid phase adsorption, nanotechnology, indigenous water treatment ways, and decentralized treatment methods will lead us to the envisaged future.

Prof. Dr. Stephen O. Ojwach – University of KwaZulu-Natal, South Africa
Prof. Dr. Chrispin Kowenje – Maseno University, Kenya
Dr. Precious N. Mahlambi – University of KwaZulu-Natal, South Africa
Prof. Dr. Gnon Baba – University of Lome, Togo

MATHEMATICAL MODELLING OF WASTEWATER TREATMENT PROCESSES, WATER ANALYSIS AND NANOTECHNOLOGY FOR DEGRADATION OF ORGANIC COMPOUNDS

Jane Catherine Ngila[1,3], A. N. Matheri[2], V. Muckoya[1], E. Ngigi[1]

[1,2]Applied Chemistry Department, University of Johannesburg, Doornfontein Campus, P.O. Box 17011, Doornfontein 2028, South Africa; jcngila2015@gmail.com; vallerie.muckoya@gmail.com; engigim@gmail.com

[3]Morendat Institute of Oil & Gas, KPC, P.O. Box 73442-00200, Nairobi, Kenya

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Abstract

Emerging contaminants in water bodies pose a health hazard to the environment and human health. Discharge of effluents from wastewater treatment plants (WWTPs) into water bodies contributes to water pollution. WWTPs face challenges in removing contaminants in real-time due to the continuously changing process parameters, diversity and pollutant concentrations. Mathematical modelling using artificial intelligence can achieve process control and optimization of programmable physical-biochemical, quantitative characterization, analysis and intelligent implementation of novel integrated waste management systems. This study aims to employ an integrated approach to WWTP design, using mathematical modelling techniques, optimised analytical methods for monitoring of the composition and concentration levels of pollutants, and nanotechnology techniques for degradation of selected organic pollutants based on tungsten oxide doped with nanoparticles. The study was carried out on a WWTP in Gauteng province, South Africa under a funded project by Water Research Commission. The modelling and computation of the speciation of compounds offered an extremely powerful tool for process design, data handling, troubleshooting and optimization of a multivariable system. The research findings on the modelling and simulation of the WWTP produced a framework that could be used in plant modelling of activated sludge and biofilm, metabolic approaches, fate of micropollutants, trace metals' removal processes and utilization of the sludge. For analysis of contaminants in the wastewater samples, multivariate-based optimization techniques for sample pre-concentration were investigated using solid phase extraction and dispersive liquid-liquid microextraction followed by chromatography-mass spectrometry techniques for quantification of parabens and polyaromatic hydrocarbons. The suitability of tungsten trioxide (WO_3) nanomaterials modified with various nanoparticles to produce iron–doped WO_3, cadmium sulphide doped WO_3, and Z-scheme cobalt oxide-tungsten oxide (Co_3O_4/WO_3) nanocomposites for the photocatalytic degradation of parabens and methylene blue were also investigated. The best photodegradation results were obtained with a Z-scheme Co_3O_4/WO_3 nanocomposite.

1 Introduction

The global population growth, economic development, urbanization, improvement in living-standards, awareness and implementation of the fourth industrial revolution *(4IR)* have increased waste generation and introduced emerging contaminants into waste streams that may pose sanitary and environmental risks [1-3]. These contaminants have increased the demand for the removal of smart-intelligent techniques for specialized emerging pollutant *(EP)* in wastewater. The emerging contaminants of concern include trace metals, personal care products, endocrine disruption chemicals, flame retardants, pesticides, pharmaceuticals, plasticizers, various fluorinated compounds, nanomaterials, etc. that have led to more stringent regulations on wastewater discharge quality parameters [4]. These contaminants end up in water bodies and landfills, leading to pollution of the environment thus putting a strain on health, economic and social sectors [5, 4]. According to [6], water scarcity in Sub-Saharan Africa (SSA) is not necessarily caused by a physical lack of water, but due to what is called "*economic water scarcity*". This means *"investments in water resources and relevant human capacity are not substantial enough to meet water demands in an area, where the population does not have the financial means to make use of an adequate water source on its own"*.

Some developing countries such as Kenya and South Africa (SA) are regarded as water-stressed nations in the world, with approximately 10% of South Africa's population being without access to safe drinking water, while in Kenya the percentage is higher and 41% of the population is without access to safe drinking water. South Africa is also among the few countries in the world that enshrines the basic right to sufficient water in its constitution of 1996. In Kenya and many other countries in the Third World and in particular SSA, due to the lack of accurate and up-to-date data, it is very difficult to do reliable estimates on the water resource requirements despite the Kenya's Natural Water Resource Management Strategy (NWRMS). Adaptive management of water could be a better way to deal with uncertainties emanating from the complex nature of issues facing resource management in Africa.

The factors affecting water scarcity in Sub-Saharan Africa include population growth, global climate change, industrial discharges into water systems, water supply misuse through illegal connections, lack of enough and dams collapsing structures in different parts in a given country, and lack of smart techniques. A good strategy to tackle these water challenges is to address sustainable water resource management, which include asset management and effective operations that call for skills and capacity in technology use, effective use and demand management, and local resource optimization such as recycled wastewater, ground water utilization, rain harvesting, water systems management and control, water re-use, desalination and utilization of sea water, and new technologies.

The aim of this paper is to explore methods of optimization of wastewater treatment plants (WWTPs) by modelling the plant design. The paper also looks at the new technologies such as analytical techniques for water analysis and nanotechnology for water treatment, especially the treated effluent water before it is discharged into the environment.

Municipal effluents collected from cities and towns should ultimately be returned to receiving water bodies after treatment, and solid waste to the land in form of fertilizers or soil amendments. The major stages in WWTPs and the units of operation, processes or methods applicable to the removal of these contaminants are well outlined [7]. The complex question that seeks to be answered relates to the nature and the extent, to which contaminants in wastewater must be removed so as to meet the set environmental standards. For safe discharge of treated wastewater back to the environment, compliance with local or international standards must be assured. Water standards include those prescribed by World Health Organization (WHO), European Water Standards, International Water Association (IWA), United State Environmental Protection Agency (US EPA), American Water Works Association (AWWA), South Africa National Standards (SANS), and Kenya Bureau of Standards, among others.

In the Gauteng province (South Africa), where the WWTP study was carried out, there are about 56 wastewater treatment plants, which are either small, medium, large or macro-sized [8]. These plants receive water that is heavily polluted with organic contaminants from different sources and of various kinds, such as polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, pharmaceuticals, polychlorinated biphenyls (PCPs), disinfection by-products (DBPs), persistent organic pollutants (POPs), and many others [9, 10]. The processes involved in treating wastewater in most of the WWTPs include sedimentation, coagulation, filtration, disinfection and advanced oxidation [11]. The disinfection process, which mostly employs chlorination in the tertiary treatment stage, has been reported to result in the formation of secondary contamination [12, 13]. The organic contaminants that accrue due to this process include DBPs, such as chlorinated methanes and acetic acid. Advanced oxidation processes such as ultraviolet combined with hydrogen peroxide treatment (UV/H_2O_2) have also been reported to enhance the formation of DBPs after post chlorination [14, 15]. The underperformance of WWTPs to completely remove these organic contaminants is expected and, therefore, the need for monitoring, identification, and rapid quantification procedures arise, followed by advanced treatment technologies. The removal efficiency of organic pollutants in WWTPs largely depends on the technology implemented. Despite advanced technologies put in place, WWTPs still experience challenges in meeting the standards for the disposal of the effluents discharged into the receiving water bodies. This is because the secondary conventional processes (trickling filters and activated sludge) that constitute the most intensely used processes were not precisely designed to remove the numerous emerging organic contaminants, leading to their partial removal from the WWTPs, and subsequent introduction into the receiving water bodies (lakes, rivers and coastal water) [16]. These receiving waters then become a source of the deteriorating surface water quality, as the WWTPs discharge into the environment is calling for monitoring the quality [17].

In order to use an integrated approach to WWTPs' process design, this project had three aspects: (1) mathematical modelling techniques, (2) analytical methods for determining the composition and quantification of concentrations levels of organic contaminants, and (3) nanotechnology techniques for photocatalytic degradation of selected organics. The project objectives were (i) development and application of mass balance equations using activated sludge model (ASM) and artificial neural network (ANN) with MATLAB (neural network toolbox) in prediction of the flow rates, organic substance levels and biomass growth, inorganics, micropollutants and trace metal speciation, (ii) development and optimization of analytical techniques for sample preparation and quantification of selected organic contaminants, and (iii) investigation of nanotechnology techniques based on tungsten oxide doped with various types of nanoparticles for possible degradation of organic contaminants in the treated water before being discharged back into the water system.

1.1 Background on methods employed

Conventional mathematical modelling, simulation and artificial intelligence / deep learning / machine learning are becoming integral components and essential to describe, to predict, to forecast and to control the complicated interactions in the wastewater treatment processes. This study used influent indices to the prediction of the effluent quality. Analytical techniques for water analysis and nanotechnology techniques based on photocatalytic degradation of organic contaminants were applied towards water treatment.

1.1.1 Mathematical modelling and design

A mathematical model can be defined as a purposeful representation or description of a system of interest towards a targeted outcome. Mathematical models are used as a simplification of reality that is relevant to understand and to apply [18]. The mathematical model of activated sludge systems usually consists of many linked algebraic and differential equation that need to be solved efficiently under different conditions. These calculations are performed by various algorithms *'solver'* that form part of the simulator's numerical *'engine'*. Mathematical models are used for research, plant optimization, plant designs, training, modelling based development and testing the process control [19]**.** A numerical model represents a real-life situation using mathematical equations. Simulation describes the use of the numerical model within a software package known as simulator [19]. Modelling can be classified into three groups: dynamic state, steady state and frozen state, where variation occurs as a function of time [18, 20].

1.1.2 Analytical techniques for monitoring water pollutants

Development and validation of novel analytical techniques, pre-concentration and determination of organic contaminants were considered. To test the robustness of the analytical system for monitoring organics in wastewater, three compounds in the class of parabens were studied, namely, methylparaben, ethylparaben and propylparaben. Sample preparation methods (extraction of the target compounds) using solid phase extraction (SPE) were studied. Analyte detection techniques based on ultra-high performance liquid chromatography coupled to tandem mass spectrometry (UHPLC-MS/MS) was investigated. Experimental factors such as sample pH, sample volume and eluent volume were optimized using a two-level (2^k) full factorial design in conjunction with response surface methodology (RSM). The chemometric approach is advantageous in that it decreases the number of experimental runs resulting in reduced analysis times, reagent consumption, sample volume as well as the cost of analysis [21]. Various extraction techniques either conventional or newly developed were employed for the determination of parabens in wastewater. They include dispersive liquid-liquid microextraction (DLLME) [22], solid phase microextraction (SPME) [23], dispersive ionic liquid (IL)-DLLME [24], magnetic solid phase extraction (MSPE) [25], and rotating disk sorptive extraction (RDSE) [21] among many others. However, the most common and robust extraction and pre-concentration method for extraction of parabens is solid phase extraction (SPE) [26, 23]. This is mainly due to its versatility in retaining these compounds and the availability of a wide array of adsorbents, chemistries and sizes of the SPE cartridges, making it a robust and selective extraction technique [27]. Liquid chromatography-tandem mass spectrometry (LC-MS/MS) is the most frequently used method for the determination of parabens due to its sensitivity, selectivity and very low detection levels (µg/L to ng/L) [28]. In addition, no derivatization is required as is the case with gas chromatography (GC) analysis [21, 29]. The UHPLC technique uses sub-2-µm particle size columns, which makes it more favourable over the traditional HPLC, as it tremendously improves resolution with increased peak capacity and shortened analysis times [30].

1.1.3 Photocatalytic degradation of water contaminants using nanomaterials

Photocatalysis is considered as one of the most promising techniques in water treatment, since it has a great potential utilizing green and sustainable solar energy in removing organic pollutants and harmful bacteria present in polluted water systems [31]. The photocatalytic technology uses light and a photocatalyst (e.g., metal oxide) in the decomposition of organic pollutants. Semiconductors have been used in photocatalysis for decomposing the organic pollutants rapidly and in an environmentally friendly manner [32-35]. Tungsten trioxide (WO_3) is a promising n–type semiconductor photocatalyst with an optical band gap (E_g) of 2.8 eV that has received attention in recent times [36, 37]. Doping of photocatalysts plays an important role in modifying the catalyst properties. Iron (Fe) was used for doping WO_3 to form Fe–doped WO_3 nanocomposite materials for the photodegradation of methylparaben as model organic substance to test the efficiency of the nano-photocatalyst using advanced oxidation process [38]. WO_3 was also doped with a metal chalcogenide, namely cadmium sulphide (with a small band gap of 2.4 eV), to form $CdS-WO_3$ for degradation of ethylparaben (EtPB) under simulated solar light. The photocatalyst employed Z-scheme nanocomposite, where two semiconductors are employed, as they exhibit better photoactivity due to suitable bandgap matching between the semiconductors. Novel Z-scheme Co_3O_4/WO_3 nanocomposite was studied for photocatalytic degradation of ethylparaben and methylene blue under visible light irradiation. Another dopant for WO_3 investigated was tricobalt tetroxide (Co_3O_4) to form Co_3O_4/WO_3, used as a novel Z–scheme photocatalyst Co_3O_4/WO_3, investigated for the photodegradation of organic pollutants, namely ethylparaben and methylene blue under simulated solar light.

2 Materials and Methods

2.1 Sampling, process design and mathematical modelling of WWTPs

Sampling of wastewater samples was undertaken from the inflow and outflow of the Daspoort WWTP, Gauteng Province, South Africa. The sampling points were division box, primary clarifier *(settler),* biological nutrients removal (BNR*)* for activated sludge WWTP or trickling filter for the biofilm WWTP, humus tank, and chlorine contact dam (CCT). Applied mass balance equations were employed, including activated-sludge model (ASM) No. 1 and artificial neural network (ANN) using MATLAB (neural network toolbox) in prediction of the flow rates, organics (substrate and biomass growth), inorganics, micropollutants concentration and their composition, biosolids utilization (biomethane production-waste to bioenergy) and sludge biochar utilization (adsorption of the trace metals in WWT). The wastewater treatment process model set-up involved translating real experimental data into a simplified mathematical description of reality. The models were used in a steady state, *i.e.,* seasonal averages *(winter and summer),* monthly simulations and yearly average performance. Figure 1 shows models' steps for the wastewater treatment.

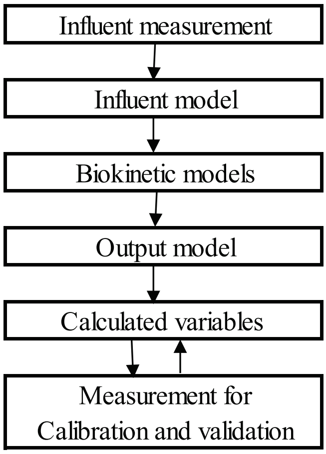

Figure 1: Overview of the modelling process

Figure 2 shows sampling location and schematic design of the Daspoort WWTP in Pretoria, Gauteng Province in South Africa, and Figure 3 is plant photo of the WWTP.

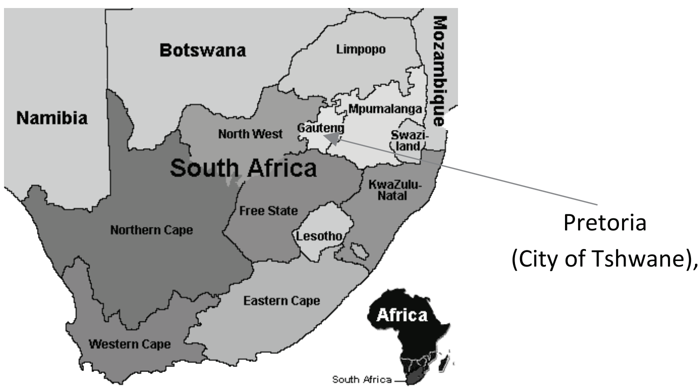

Figure 2: Map of Daspoort wastewater treatment plant at Gauteng Province, City of Tshwane, South Africa

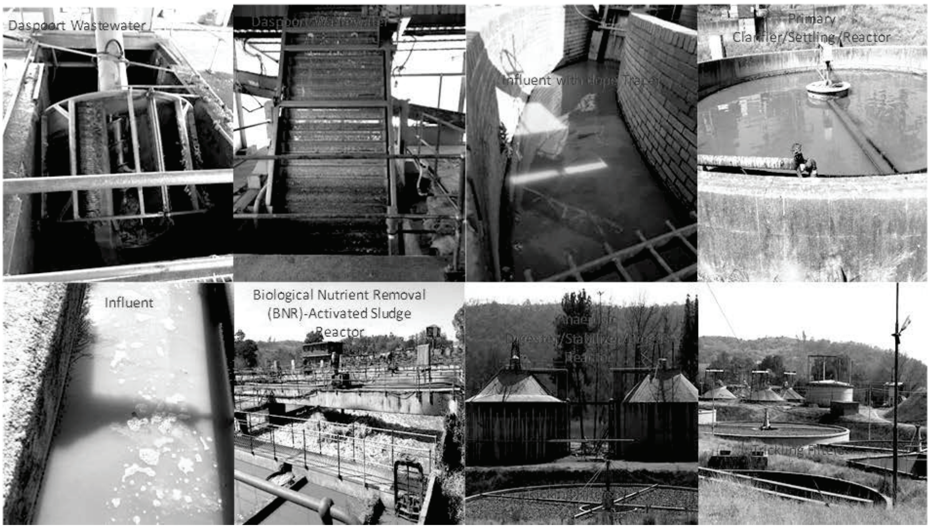

Figure 3: Photos of the Daspoort WWTP

Modelling process included decisions on the model layout, sum-models structure, setting up models, output graphs and tables. The analyses of the raw influent and performance data of the historical plant were carried out for the period of 2015-2017 to establish the WWTP performance and efficiency. An excel spreadsheet was developed for data recording. Modelling and simulation were carried out by computation tools like Aquasim, ChemCad, DynoChem, Aspen-Plus, IWA cost benchmark, Matlab Simulink, SPSS, python, and Simba. Model layout involved translating of existing process flow scheme and mixed behaviour into model concept. Modelled process units were each selected and connected to the sub-models. Mass balance was used to detect the inconsistencies within the WWTP datasets through identification and confirmation of the mass flow into and out of the systems. The model approach was based on different levels of simplification of the real system, but are both justified by accepted scientific and engineering principles.

Materials used for the wastewater analyses include plastic sample bottles of 500 mL capacity used to collect samples. Tracer detectors (LiCl and Li_2CO_3), fluorescein sodium salt, FSS ($C_{20}H_{10}O_5Na_2$:376.27), and injector were used to establish the residence time distribution for the fluid and sludge. A microwave and hotplate were used in the digestion of the samples. A membrane filter (pore diameter 0.22 µm) was used to filter the samples before analysis. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used for trace metals analysis. Organic compounds-micro pollutants were analysed using gas/liquid chromatograph coupled to various detectors such as the mass spectrometer (GC-MS and LC-MS) and with high-performance liquid chromatograph (HP-LC) with a UV detector. Chemical Oxygen Demand (COD) was analysed using spectrophotometer from Hach. Vials were used to hold liquid samples for analysis. Digital pH meter with electrodes for measuring temperature and electrical conductivity (EC) were used to analyse pH, temperature and EC, respectively, of wastewater treatment on-site.

Mass balance was an engineering tool that allowed the identification and confirmation of the mass flow into and out of a processing system based on a mass conservation principle. Open and closed mass balance was applied. The measured influent organic and suspended input data (influent wastewater characteristics) for the WWTP mass balance included chemical oxygen demand (COD), nitrogen compounds (i.e., N_2, N_2O, NO_X-N, NH_X-N, TKN), phosphorus $P_{tot,}$ (ortho-phosphate PO_4^{3-}), volatile fatty acids (VFA), total suspended solids (TSS), chlorine (Cl_2) and trace metals. The physically measured data (operation variables) were tank volume, depth and layouts, flow connections and hydraulic behaviours and flow rates. The performance measured data were effluent organics, effluent nutrients, mixed liquor (MLSS and MLVSS), dissolved oxygen (DO), temperature, pH, alkalinity, and ortho-phosphate. The total suspended solids (TSS) denoted as X_{TSS} consisted of volatile suspended solids (VSS). The inorganic suspended solids ISS was described by (ISS = TSS -VSS). Alkalinity was introduced to the models to predict possible pH changes and to guarantee the continuity in the ionic charge of the biological processes.

Dynamic models are useful in prediction of time-dependent systems response of an existing or proposed system. Dynamic model guide in the development of the steady-state design models by identifying the design parameters that have a major influence on the system response [18]. WWTP models are used to indicate the ensemble of the activated sludge models, oxygen transfer model, hydraulic model and sedimentation tank model reported by Gernaey et al. [39]**.** These models include: (i) primary settlement sizing and velocity, which defines the particle settling velocity, (ii) the organic volumetric loading rate, applied to the aeration tank volume per day in terms of COD, (iii) sludge retention time or sludge age, which impacts the solids production on the operation and design parameters for activated sludge processes; (iv) specific organic loading rate defining the specific organic loading rate to a maximum organic removal rate used as an indicator of stability, (v) the effect of temperature on the metabolic activities of the microbial population on a wastewater biological and chemical reaction-rate constant, (vi) effect of pH on metabolism, which defines the pH of the wastewater treatment system, modelled on a range of 7.2 to 9.5, (vii) biomass concentration mass balance determined as a function of sludge retention time in the aeration tank hydraulic retention time, (viii) the substrate mass balance for the complete mix activated sludge process as a function of time and the kinetic coefficient for the growth and decay, (ix) mixed liquor solids concentration and solids production quantified in terms of the total suspended solids, volatile suspended solids, biomass and sludge retention time, which provided a convenient expression to calculate the total sludge produced daily from the activated sludge process, (x) the biological nitrogen removal through nitrification, modelled on activated sludge system in a single completely mixed reactor system with a hydraulic control of sludge age, (xi) oxygen demand mass balance, the oxygen required for the biodegradation of carbonaceous material determined from a mass balance using COD concentration of the wastewater treated and the amount of biomass wasted from the system per day, (xii) biological removal of recalcitrant and trace organic compounds, which is the mass balance for the biological removal of emerging organic compounds (emerging micro-pollutants) that resist conventional biodegradation in biological treatment processes, (xiii) disinfectants used in the wastewater treatment in terms of pathogens (fungi, viruses, helminth, protozoan oocysts, bacteria) were removed in the effluent by the application of disinfectants, chlorine. The chemical disinfectant kinetics of the chlorine was based on the pseudo-first order decay rate constants, (xiv) food to microorganism ratio; food to microorganism ratio was defined as the rate of COD and applied per unit mixed liquor, (xv) removal efficiency of the organic compounds, which is the process removal efficiency is defined as percent COD across the activated sludge system.

Calibration and validation of mathematical models were introduced for elucidating the mechanisms of the activated sludge processes. The models were adjusted after calibration with the set of influent experimental data to allow process modification of the input data until the simulation model results match the influent data set. The effluent results were counter checked for compliance with South Africa Department of Water & Sanitation, Wastewater Treatment License. Modelling analysis was done using microbial growth kinetics, mass balance, and activated sludge model no. 1 of the WWTP.

2.2 Sample collection for analytical techniques

The analytical procedures used for sample preparation and quantification of the organic contaminants in wastewater included sample collection, solid phase extraction (SPE), experimental design, and application of carbon nanodots in SPE. The quantification techniques included liquid chromatography and gas chromatography coupled to tandem mass spectrometry. Chemometric techniques were used for the optimization of sample extraction procedures as per Muckoya et al. [40]. The collection of samples from WWTP in Gauteng was done from two locations in the east and west of the plant. There were 7 sampling sites from the east plant and 6 sampling sites from the west plant. Two samples were collected per sampling site, while observing the retention times calculated by the use of the tracer [41]. Solid phase extraction procedure: Extraction of parabens from the wastewater samples was performed using Oasis HLB cartridges (6 mL, 200 mg). Prior to the extraction, the samples were filtered on a Millipore filtration unit using 0.45 µm filter paper to remove any suspended matter that may otherwise interfere with the SPE extraction due to clogging. A multivariate experimental design was employed for optimization of SPE experimental conditions [42]. The parameters studied were sample volume, elution volume and sample pH, and solid phase extraction of parabens with packed carbon nanodots (CNDs). Characterization of synthesized CNDs was done with TEM, SEM, FTIR, XRD techniques. The carbon nanodots were synthesized according to previous literature [43] with slight modification as per Muckoya et al. [51]. The application of the CNDs for extraction of methyl-, ethyl- and propyl paraben (MePB, EtPB, PrPB), azinphos-methyl and parathion-methyl from the wastewater samples was performed using pre-packed SPE cartridges with the CNDs. Liquid chromatography - mass spectrometry experimental runs were conducted using Nexera Ultra High-Performance Liquid Chromatography (UHPLC Shimadzu, Japan). Separation of the analytes was obtained using a pinnacle DB biphenyl column of 100 x 2.1 mm and 3 µm particle size (RESTEK, USA). The mass spectrometry detection