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Editorial

Innovative Approaches for Drinking- and Waste-Water Treatment: An Editorial Review Summarizing and Assessing the Findings of the Special Issue

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Abstract: The present special issue collected articles that address the very important topic of innovative approaches in water and wastewater treatment technologies. Thirteen articles are published, ten research paper and three review articles. The papers can be divided in four major categories, namely, membrane treatment, adsorption studies, advanced oxidation processes and wastewater treatment optimization. In the editorial, a brief description of the findings of each paper is presented along with a critical assessment.

Keywords: arsenic; chromium; uranium; graphene; energy conversion; sewage sludge; minimization; green technologies; chitosan; Fenton

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1. Introduction

The present special issue comprises a collection of recent research accomplishments from well recognized scientists in the field of water science and technology, aiming at assembling contributions on advanced technologies that have been applied to the treatment of waste- and drinking water. Thirteen published research contributions highlighted various processes and technologies that can achieve the effective treatment and purification of natural or engineered aquatic systems. Ten papers reported original research findings and three papers reviewed relevant topics.

The published papers can be classified into four major categories. (a) First, there are those that investigate the application of membrane treatment processes, either directly [1] (b) second, there are studies that investigate the application of adsorptive processes for the removal of contaminants from waters, such as arsenic, lead, nickel or chromate [2–6], but also assessed the health effects of their exposure to humans [7]. (c) third, there are studies that include novel aspects of oxidative treatment [8,9] and (d) fourth, studies that examine wastewater treatment efficiency, testing new type reactors [10], minimizing the sewage sludge [11] or energy minimization and conversion and in wastewater treatment facilities [12,13].

2. Results

Zhang and co-authors [1] prepared and investigated the use of polyvinyl alcohol/bacterial cellulose/biochar–nanosilver (PVA/BC/C-Ag) antibacterial composite membrane materials by uniformly dispersing C-Ag particles in a PVA/BC mixed gel. Their findings indicated that the BC was consistently mixed into the PVA gel and that the C-Ag particles were evenly immobilized in the PVA/BC hybrid membrane. The PVA/BC/C-Ag composite membranes displayed exceptional antibacterial activity against *Escherichia coli*. In the treatment of contaminated water, the composite membranes demonstrated sustained antibacterial activity

and good reusability. This study highlights the importance of investigating materials that show antibacterial activity, which is a very important topic in water treatment, especially with emphasis when water reuse is aimed [14].

In the group of adsorption studies, Muhammad and co-authors [2] reported on the synthesis, characterization, and utilization of polyaniline (PANI) and its composites with Fe_3O_4 for the removal of hexavalent chromium Cr(VI) and divalent nickel Ni(II) ions from water. The authors tested Freudlich, Langmuir, Tempkin, Dubbanin–Ruddishkawich (D–R), and Elovich adsorption isotherms for the description of the process and found that the Freundlich isotherm fits more closely. Various other parameters were investigated, such as the solution pH, initial concentration, contact time, ionic strength, and adsorbent dosage on adsorption behavior were investigated. Uptake of Cr(VI) on all the materials was high in an acidic environment while that of Ni(II) was optimum in a slightly basic environment. Competition by co-existing anions was observed. In particular, removal of $HCrO_4^-$ was competed with by HSO_4^- in acidic environments while that of Ni(II) was competed with by Na^+ ions when the solution was slightly basic. The maximum amount of Cr(VI) adsorbed by PANI/Fe_3O_4 composites was 174.09 mg·g^{-1}, while that of Ni(II) was 134.88 mg·g^{-1}. The kinetics of adsorption was pseudo-second order. The negative sign with the values of Gibb's free energy changes and enthalpy and entropy changes confirmed the spontaneous and exothermic nature of adsorption.

A second study tested the removal of hexavalent chromium and reported the results in the present special issue. Katsoyiannis and co-authors examined the use of a pipe flocculation reactor, followed by sand filtration. Ferrous sulphate was dosed in an inline mode to the Cr(VI) contaminated groundwater and through an oxidation reduction reaction, Cr(VI) was reduced to Cr(III), which was then adsorbed in the formed iron oxides and removed through sand filtration [3], in agreement with previous studies, which demonstrated by using XPS analysis [15]. Experiments were conducted at pH 7.2, using Thessaloniki tap water, which has a typical composition of a groundwater. The water was spiked with Cr(VI) at various concentrations. The required ratio of [Fe]/[Cr] for an efficient Cr(VI) removal, at pH 7.2 was slightly above 10, much above the stoichiometry of the reaction between Fe(II) and Cr(VI). Previous relevant studies accomplished in batch mode [16] have demonstrated that the main reason for this difference is the competition of this reaction by oxygen. Oxygen reacts also with Fe(II) and the kinetics of Fe(II) oxidation by oxygen increase as pH increases above pH 7 [17].

Wei et al. [4] in their study managed to improve the adsorption and separation efficiency of lead-containing wastewaters by graphene oxide (GO), which was used through a simple hydrothermal reaction. The prepared GO was characterized by SEM, TEM, FTIR, and XPS. The adsorption characteristics of the prepared GO were studied and found that the maximum adsorption capacity of Pb^{2+} on GO at pH 5 and 25 °C was 450.9 mg/g.

In a next study [5] arsenic, manganese, zinc, cadmium and lead removal from aqueous solutions was investigated by the use of sludge, resulting from an iron-ore processing area. The adsorption capacity of target adsorbates was investigated in batch experiments of both single- and mixed-metal solutions. The results demonstrated that the maximum Langmuir adsorption capacities of the heavy metals onto the adsorbent occurred in the order Pb > As > Cd > Zn > Mn, and ranged from 0.710 mg/g to 1.113 mg/g in the single-metal solutions and from 0.370 mg/g to 1.059 mg/g in the mixed-metal solutions. Adsorption performances indicated that iron-ore sludge can simultaneously adsorb multiple metal ions and is a promising adsorbent for the removal of toxic pollutants from water, since there are several cases, where multiple heavy metal pollution of waters occurs and to remove them from waters, there is a need for adsorbents able to remove several contaminants simultaneously.

The article by Tolkou et al., [6] summarizes the recent findings regarding the removal of arsenic, chromium and uranium by novel composite hybrid materials, with emphasis in the use of novel composite materials, based mainly on hybrid metallic oxide nanoparticles and on composites based on graphene oxide (GO) (i.e., graphene-based hybrids). Particularly, for the removal of arsenic, it was reviewed the application of hierarchically porous CeO_2–

ZrO_2 nanospheres, the bimetallic mixed oxide (NHITO), and the copper(II) binary oxide nanomaterials and graphene based, such as graphene oxide-ferric hydroxide GO/$Fe(OH)_3$ composites, magnetite Fe_3O_4-reduced graphite oxide–MnO_2 and graphene oxide-hydrated zirconium oxide. Among these materials, the iron(III)-copper(II) binary oxide, showed particularly high adsorption capacities for both As(III) and As(V) of 122 and 83 mg/g respectively. This material was more efficient for As(III) removal than for As(V), which suggests that it might be very useful in the treatment of anoxic arsenic contaminated groundwaters, which contain mostly As(III) [11]. In these cases usually a peroxidation step is required, unless if As(III) efficient adsorbent are developed, such as the one in this study, or others, such as the use of polyferric sulfate [18] or Aquaszero [19,20].

Regarding chromium removal, the application composite graphene based materials, such as Graphene Oxide Functionalized with Magnetic Cyclodextrin–Chitosan (CS-GO), Poly-Pyrrole Graphene Oxide Nanocomposite (PPy–GO-NC), and Graphene Oxide/Poly-Amido-Amine Dendrimer (GO/PAMAMs) were found very efficient for the adsorption/removal of Cr(VI), presenting adsorption capacities of 104, 625, and 211 mg/g respectively [6]. However, these values were recorded only at pH values below 5 and, therefore, they could find applications for the treatment of acidic wastewaters, avoiding the usually applied preliminary reduction step towards the Cr(III) formation.

With respect to uranium removal, the review highlighted the use of magnetic Fe_3O_4@SiO_2 composite particles, as well as off several novel graphene modified composite materials, such as Three-Dimensional Layered Double Hydroxide-Graphene Hybrid Material (rGO/LDH), Novel Graphene Oxide-Activated Carbon Felt Composite (GO-ACF), Graphene Oxide and Its Amine-Functionalized Composite (GO-NH_2) which showed promising results with reported adsorption capacities as high as 278, 298 and 215 mg/g, which are very good results when compared to conventional adsorbents such as iron oxides [21], which show capacities between 100 and 135 mg/g.

The next paper [7] focused on the contents of the five most bio-toxic heavy metals, As, Cd, Hg, Cr, and Pb in samples from 26 municipal solid waste (MSW) from the Eastern Guangdong Area. Pearson correlation and principal component analysis (PCA) were introduced as major approaches and health risks posed to MSW workers exposed to heavy metals in MSW were assessed using a Monte Carlo simulation combined with the US Environmental Protection Agency Health Risk Assessment Model. The results showed that As, Cd, Hg, Cr, and Pb contents of the east Guangdong MSW were (0.76 ± 0.75), (2.14 ± 4.44), (0.11 ± 0.14), (55.42 ± 31.88), and (30.67 ± 20.58) mg/kg, respectively. Hg, Cr, and Pb were most likely originating from glass, textile and food waste, whereas As and Cd were mostly coming from soil and food waste in the MSW. The study highlighted that the heavy metals in MSW might induce carcinogenic risks, with the likelihoods for male and female workers being 35% and 45%, respectively.

In the subject of advanced oxidation processes, this special issue contains two very interesting articles, reporting recent developments in the field, highlighting potential applications in water and wastewater treatment. The first study [8] depicted the comparative performance of micropollutants' removal by $FeSO_4$- and zero-valent iron (Fe(0))-catalytic Fenton oxidation explored the possibilities of minimizing the sludge production from the processes. The emerging micropollutants examined in this paper were gabapentin, sulfamethoxazole, diuron, terbutryn and terbuthylazine. Both $FeSO_4$- and Fe(0)-catalytic Fenton oxidation were able to completely degrade the stated micropollutants. The Fe(0)-catalytic Fenton process accomplished better removal of dissolved organic carbon (DOC; 70%) than $FeSO_4$ catalytic Fenton oxidation (45%).

The second study in this field, [9] used sodium hydroxide-modified graphene oxide to support manganese oxides aiming at the formation of nanocomposites via a one-pot preparation route for the degradation of Reactive Black 5. The nanocomposites were characterized by X-ray diffraction, nitrogen adsorption, Fourier transform infrared spectroscopy, potentiometric titration, and thermal analysis measurements. The nanocomposites shoed high activity for the abatement of Reactive Black 5 at ambient conditions, without light

irradiation. The study concluded that RB5 degradation was mainly based on the release of H_2, the cleavage of -N=N- bonds and the formation of -NH_2 groups. The presence of H_2O_2 could increase the RB5 degradation by producing hydroxyl radicals which are able to decompose the dye molecules.

The field of wastewater treatment is covered by four articles in this special issue. The first article, [10] reported the development of a pilot-scale six-compartment hybrid anaerobic baffled reactor (HABR) with effective volume of 18 m^3 for the treatment of dyeing wastewater. The HABR system treated effectively the wastewater after pretreatment with FeSO4. This was shown considering the removal efficiencies of 33.7% for chemical oxygen demand (COD), 39.9% for suspended solid (SS), and 22.5% for sulfate (SO_4^{2-}) during a steady state operational period. Besides, it was found that the concentrations of several categories of organic compounds, such as alkanes, amides, organic acids, ketones, phenols, and esters were much lower in the effluent than those in the influent. In addition, many high-molecular-weight compounds such as cyclanes, quinolines, and phenols were successfully transformed to low-molecular-weight compounds. Based on the overall treating effectiveness, the optimized operation plan of the wastewater treatment by HABR was achieved as the hydraulic retention time (HRT) of 12 h for steady-state operation with an up-flow velocity of 1.7 m/h as well as OLR of 1.5–2.0 kg COD/(m^3·d)

Next, Collivignarelli and co-authors [11] reviewed the strategies for minimization of sewage sludge from wastewater treatment plants. In general, sewage sludge production (SS) should be reduced, not only because of restrictions imposed by the European Directive 2018/851 on waste, but also because the cost of sludge management accounts approximately for 50% of the total running costs of a wastewater treatment plant (WWTP). Minimization technologies adopt the following strategies: (i) implementing a process in the water line that reduces the production of sludge; (ii) decreasing the water content (dewatering processes) or (iii) lowering the portion of volatile solids (stabilization). This review was based on more than 130 papers and provided significant information on the process, such as the advantages, the drawbacks and the results of their application. Furthermore, information on the technologies that are still under progress is provided. Finally, this review assesses the impact of the application of the proposed processes in the sludge line on a WWTP, for cases with a capacity exceeding 100,000 population equivalent (PE).

In a similar context, Sun et al., [12] reported on the application and evaluation of energy conversion technologies in wastewater treatment plants. The reason is that high energy consumption is a critical issue influencing the operation and sustainability of wastewater treatment plants (WWTPs). This paper seeks energy-saving opportunities from three aspects: energy application, process improvement, and performing assessment. Furthermore, effective energy-saving can be accomplished from the perspective of energy supply and recovery by using green energy technologies. System optimization and control is used to reduce unnecessary energy consumption in operation. Various indices and methods can assist researchers to assess the application value of energy-saving technologies. This work can give engineers some suggestions about reducing energy consumption from comprehensive perspectives.

Finally, Piotrowski and co-authors [13] studied the optimization of biological processes in the course of wastewater treatment in sequencing batch reactor (SBR) plant. In their study, an optimizing supervisory controller generated the dissolved oxygen (DO) trajectory for the lower level parts of the hierarchical control system. The main goal of the study was to reduce the plant energy consumption and to maintain the quality of effluent in compliance with the legislative limits. The authors performed simulation tests and decided to implement a hybrid process of two different optimization algorithms: artificial bee colony (ABC) and direct search algorithm (DSA). Simulation tests for the wastewater treatment plant case study were presented.

3. Conclusions

With more than 2 billion people worldwide suffering from water scarcity, clean water is one of the most important natural resources on earth, whereas wastewater, corresponding to spent water, can be considered as a valuable natural resource, if treated and reused. 13 articles published in this special issue report on the development of novel technologies to achieve optimized water and wastewater treatment, with the aim to tackle in the future water shortage related issues. We hope that these articles offer important insight in environmental problems and besides the scientific interest; they can also promote awareness to authorities regarding the intensification of research and possible solutions to these problems.

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