sustainability.

Looking ahead, first principles modeling of contaminant adsorption in water, holds great promise for addressing global water challenges. By leveraging the predictive power of DFT simulations and interdisciplinary collaboration, researchers are developing next-generation water purification technologies.

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Guest Articles

Electrospun nanocomposite fibers for the adsorption removal of antibiotics from water bodies

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1. Introduction

In the recent past, the overuse of antibiotics in various disciplines such as medicine (cancer treatment, heart surgery, and organ transplant), agriculture, and animal husbandry has led to the excess discharge of antibiotics from their working environments to the various water bodies, posing a major threat to both public health and the ecosystem.[1] However, the ability of antibiotics to act effectively against a wide array of microbial strains has made them the best choice to mitigate the problem of microbes in many fields.[2]

Antibiotics are typically abundant in sewage and then enter to the wastewater treatment plants. Even though the wastewater plants could remove nitrogen (N), phosphorus (P), and chemical oxygen demand (COD), they have been incapable of removing the antibiotics present, therefore they are found to be present in 10-3000 ng/L range in the secondary effluents.[1] Furthermore, they are also found to be abundant in surface water, groundwater, seawater, drinking water, and sediments.[3] However, their distribution is typically high in hospital sewage accounting for values in the range of mg/L.[4] Albeit these amounts have appeared to be very low, the impact it could create is significant and considerable. As they have very complex structures, high stability, and lower degradability they have become persistent as micropollutants in wastewater.[5] It is a well-identified fact that antibiotics could also reach the water bodies *via* the feces and urine of humans and animals, direct contamination from pharmaceutical discharge from production plants, and discharge from aquaculture plants.[6]

According to recent reports, about 21 antibiotics with concentrations ranging from 5800 ng/g are found to be present in different wastewater treatment plants4 where the commonly identified antibiotics from water bodies include quinolones, sulfonamides, tetracyclines, beta-lactams, trimethoprim, and macrolides, which are frequently used in medical treatments.[1] The abundance of antibiotics in water bodies has been identified in various parts of the world including Vietnam, United States, South Korea, Canada, China, Hong Kong, Greece, England, and India[7] where some studies have indicated the appearance of them in the Sri Lankan context such as in Kaleni and Gin river.[8]

2 Environmental and health impacts of antibiotic pollution

As these antibiotics cannot be fully absorbed by the human or animal body, it is estimated that 10-90% of the content is discharged into the environment as the mother compound or as byproducts. Because these compounds are highly resistant to degradation and remain stable over some time, they can induce antibiotic resistance in various bacterial species present in aquatic environments. Consequently, this has contributed to the development of antibiotic resistance over the common antibiotics and the translocation of the genes among different strains promoting a pool of mutli-drug resistant or antimicrobial-resistant (AMR) bacteria. AMR is considered one of the key problems in the 21st century. The ultimate result has been the poor effectiveness of conventional antibiotics and the prevalence of certain infectious diseases among the population left with no cure.[6]

However, studying the impact of the spread of AMR in the environment has received less attention compared to the consideration given to animals and humans. The release of antibiotics into the ecosystems and the bioaccumulation through the food chains could allow long-term changes in the genetic makeup of naturally occurring bacteria and aquatic organisms allowing the emergence of many more resistant strains.[5,6]

In addition, these antibiotic compounds could also amalgamate with other pollutants in the water bodies and would lead to the generation of highly toxic compounds with deleterious effects. This highlights that the prevalence of antibiotics being unattended causes a serious threat to human health and to the stability of the ecosystem.[1] Therefore, the removal of these contaminants from the water bodies has become a hotspot in environmental research.[9]

3 Current methods for antibiotic removal

The available content of the freshwater for usage accounts only for 3% of the total amount of water on the planet. Further, the World Watch Institute has estimated that the poor quality of water and the water shortage is likely to affect nearly 2/3 of the world's population by the year 2025, where the impact could be on the human population representing every country of the planet. Therefore the treatment of sewage and wastewater have been left as the only remaining option to cover the developing demand for the freshwater.[4]

Over the last few decades, numerous techniques have been utilized for the removal of organic contaminants present in water bodies. They include coagulation and sedimentation, biodegradation, disinfection by chlorine, advanced oxidation (AOP) processes, photocatalysis, degradation by electron beam, ozone, nanomembrane filtration, and adsorption removal. Among these techniques, AOP has been an expensive method for the large-scale removal of antibiotics while the biodegradation-like techniques have not demonstrated much of an effective and efficient removal of antibiotics. These findings suggest that adsorption removal could be considered the most effective technique for antibiotic removal due to its operational simplicity, cost-effectiveness, and ease of application.[7]

The adsorption removal of a compound can be described as an adhesion process on a liquid, solid, or gas phase on the surface of another material. Here the material that is getting adsorbed is considered to be the adsorbate whereas the material that is used to remove the contaminating material is called the adsorbent.[10]

The typical absorbent material used for the removal of antibiotics include porous materials like activated carbon, zeolite, mesoporous silica, bamboo-based carbon, graphene oxide composites, sawdust, fly ash, hydrogels, metal oxides, kaolinite[7], metal organic frames.[11] However, these materials have displayed unsatisfactory removal efficiencies mainly due to the poor binding with the adsorbate. Therefore the development of new material for antibiotic removal has been a considerable research interest in recent years. Further, this has also led to the spreading of antimicrobial-resistant genes among the organisms.[6]

4 Electrospinning technique

The electrospinning technique is one of the promising fabrication techniques, leading to the formation of nanofibrous membranes with interconnected nano or microporosity accounting for high surface area and better mechanical properties. These fibers are massively applied in fields like medicine, energy, water treatment and agricultural food production to obtain improved performances. Additionally, these materials possess the ability to combine with other advanced materials leading to enhanced mechanical and physicochemical properties thereby opening avenues for new research exploration.

The resulting fibers are generally continuous woven or non-woven fibers with micro or nanostructure. In a typical electrospinning process, it allows the interaction of the polymer solution with the electric field being supplied. The voltage difference leads to the formation of an uncompensated charge accumulation on the polymer surface, and when the polymer solution is pumped through the needle, a strong repulsive charge on the polymer surface is developed which could exceed the surface tension and the viscous forces at some point. As indicated in Figure 1, it leads to the formation of a conical shape droplet formation from the polymer at the needle tip which is called as the "Taylor cone" that quickly expels and leads to the formation of a polymer jet. This jet is accelerated towards the conductive collector while the solvent is being evaporated during the traveling of the polymer jet. The intermolecular interaction among the polymer molecules allows the deposition of the solid matter as a non-woven mesh over the collector surface. The correct formation of the nanofibers extensively depends on some process parameters such as voltage, the distance of traveling, flow rate, and the diameter of the needle/spinneret. Furthermore, the polymer parameters such as concentration, viscosity, molecular weight, and conductivity also play a critical role in defining the proper formation of beadless nanofibers.[10] In addition, the environmental parameters such as the temperature and the humidity also have a direct link to the formation of the nanofibers as reported in previous work.[12] It is a key requirement to finetune the above-mentioned factors for the proper fabrication of the nanofibers which ultimately determines the overall applicability of them on the adsorption removal of contaminants.

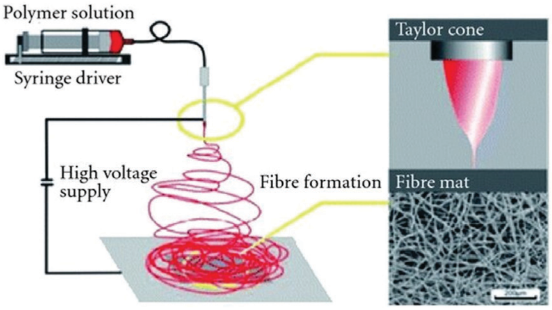

Figure 1: Electrospinning set up, Taylor cone formation leading to nanofiber generation (Reprinted with permission from Pillay *et al.*, 2013, Copyrights from Elsevier).

5 Nanocomposite nanofibrous materials for antibiotic removal

There are some reported studies have focused on the use of electrospun nanofibers for the removal of certain antibiotics like tetracycline using TiO_2@g-C_3N_4 (TCN) incorporated poly (vinylidene fluoride) (PVDF)[13], Sulfamethoxazole (SMZ), sulfamethazine (SM2), trimethoprim (TMP), erythromycin (EM), tetracycline (TC) and, chloramphenicol using nanocomposite membranes (CL)[14], copper sulfide nanoparticles (CuS NPs)/chitosan nanofiber composites for the removal of tetracyclin[15], heterostructured g-C_3N_4@Co-TiO_2 (CNCT) nanofibrous membranes for the removal of tetracyclin[9] and the β-FeOOH, β-FeOOH/TiO_2 incorporated cellulose acetate nanofibers for the removal of Doxycycline (DC).[5]

Much of these reported work have focused on the removal of antibiotics with the use of NF, where the primary mechanisms of removal have been photocatalytic degradation[5,9,13,15] osmotic removal[14], electrocatalytic removal[16] among others. Nevertheless, the use of composite ENF for adsorption removal is seldom where the application has been restricted only for a few studies. In the work conducted by Das *et al.*, montmorillonite-impregnated cellulose acetate nanofiber membranes (MMT-CA-NFM) have been employed for the removal of ciprofloxacin (CIP), with a removal percentage of 76% over 60 minutes. This composite NF has accounted for a sorption capacity of 13.8 mg/g while expelling its ability to perform as a reusable nanofiber membrane for several rounds of purification.[7]

As depicted in Figure 2., Zhao *et al.*, have explored the possibility of using adsorption mesoporous channels created with the use of a nanohybrid made out of MOF-infused electrospun nanofibers for the removal of tetracyclin from water. The hybrid was a construct of electrospun zeolitic imidazole framework -8 (ZIF-8) with polyvinyl pyrrolidone (PVP) guided polyacrylonitrile (PAN) fibers. It has been observed that this mesoporous interconnected channel would lead to an adsorption capacity of 885.24 mg/g of tetracycline while accounting for the removal efficiency of 97%. Furthermore, the material suggested here was capable of performing up to 10 adsorption-desorption cycles.[11]

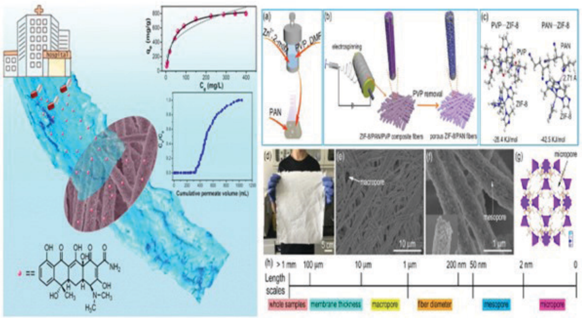

Figure 2. Schematic illustration of electrospinning solution preparation for MOF-infused electrospun nanofibers for tetracycline removal (a) and fiber preparation (b), (c) Optimized geometries for the configuration of PVP and PAN with the ZIF-8 fragment. Corresponding optical (d) and SEM images (e, f, the inset is the cross-sectional image) of porous ZIF-8/PAN fibers. (g) Structure of ZIF-8. (h) Schematic of the levels of hierarchical size scales (Reprinted with permission from Zhao *et al.*, 2021, Copyrights from Elsevier).

On a similar note, the work carried out by Wang *et al.*, has fabricated a novel composite carbon nanofiber (CNF) containing CNFs and β-cyclodextrin based carbon nanoparticles (CNPs) created via electrospinning technique and hydrothermal process. The resulting composite material with a high surface area (3561.59 m^2/g^{-1}) and larger pore volume (4.78 cm^3/g^{-1}) has been effective in effective adsorptive removal of tetracyclin while accounting for an adsorption capacity of 543.48 mg/g. Further, this study claims that the developed material could be reused for five effective cycles without any retardation of the adsorption removal capacity.[17]

Besides, the ENF composites made out of Fe_3O_4-incorporated polyacrylonitrile (PAN) have been also employed for the effective removal of tetracyclines from wastewater. `The X-ray diffraction studies, as well as field emission scanning electron microscopy, have confirmed that the Fe_3O_4 nanoparticles are well deposited as a surface coating on the PAN nanofibers where this pattern of deposition has been effective on the removal of the antibiotic with a maximum adsorption capacity of 315.31 mg/g. Furthermore, the magnetic responsiveness of the NF mat has allowed the easily separable option of the adsorbent after the adsorption process, making it convenient for the removal of micropollutants.[18]

Similar approaches have been also taken for the removal of tetracycline from wastewater using recyclable, polydopamine coating assisted zeolitic imidazolate framework-8 (ZIF-8) functionalized composite PAN (ZIF-8/PDA/PAN) nano adsorbent accounting for a removal efficiency of 85%3. More information related to the adsorption removal via the composite ENF can be obtained from the review articles published in this regard.[4]

6 Adsorption isotherms and kinetics

To predict the adsorption removal mechanism, the interactive behavior of the adsorbent and the adsorbate at constant temperature and pH is evaluated. Here each adsorption process is described via a mathematical model. The parameters that are being considered to compare the behavior of different systems include the initial concentration of the adsorbate (C0), the remaining concentration at time t (Ct) and the equilibrium concentration (Ce). The best-fitted model could explain the adsorption mechanism and generally Langmuir and Freundlich isotherms are used to describe the behavior of the adsorption process. On the other hand, kinetic models are being employed to predict the chemical rate and the chemical rate-determining step during the adsorption process. The commonly applied ones include the pseudo-first-order and pseudo-second-order. For more information, a reader could kindly refer to the following articles.[10,17]

7 Challenges and Future Prospects

Even though nanocomposite electrospun nanofibers have proven to be effective as a potential material in removing antibiotics from water bodies, some limitations have been noticed such as the improper pore size to facilitate proper adsorption.[10] Furthermore, challenges like poor efficiency of the materials, and high-cost of production impairing the scalability remain to affect the successful implementation of these materials in the successful removal of the antibiotics in practical terms.

However, research on improved surveillance approaches leading to eco-friendly smart composite nanofibers with excellent adsorption capacities, and structural integrity will guarantee the efficacious treatment of water bodies. This will help to curb the menace of the development of AMR and safeguard public health and environmental conservation.

Conclusions

As a summary of the article, it can be concluded that the widespread presence of antibiotics in aquatic environments is a crucial public health and environmental issue due to the emergence of AMR. Traditional treatment approaches such as coagulation and sedimentation, biodegradation, disinfection by chlorine, advanced oxidation (AOP) processes, photocatalysis, degradation by electron beam, ozone, and nanomembrane filtration have proven to be ineffective in removing micropollutants such as antibiotics. However, the adsorption removal via composite nanofibers is proven to act as potential adsorbent materials providing better adsorption capacities together with their reusable ability. Further advancement of these nanofiber materials with additional properties is expected to improve the effectiveness of the adsorption removal of antibiotics from water bodies on a larger scale promoting the sustainable approaches in decontamination of waterbodies. This will help obtain the "One Health Approach (sustainably balance and optimize the health of people, animals and ecosystems)" proposed by the World Health Organization (WHO).

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