



Anal. Bioanal. Chem. Res., Vol. 3, No. 1, 1-18, June 2016.

Removal of Pharmaceutical Compounds from Hospital Wastewaters Using Nanomaterials: A Review

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(Received 12 October 2015, Accepted 3 January 2016)

Over the past few years, residual pharmaceuticals (antibiotics, anticonvulsants, antipyretics drugs, hormones) have begun to be considered as emerging environmental pollutants due to their continuous input and persistence to aquatic ecosystem even at low concentrations. Therefore, the development of efficient, cost-effective, and stable methods and materials for the wastewaters treatment have gained more recognition in recent years. In the path of meeting these developments, nanomaterials have attracted much attention as economical, convenient and ecofriendly tools for removing of pharmaceuticals from the hospital wastewaters because of their unique properties. The present review deals with recent advances in removal and/or destruction of residual pharmaceutical in wastewater samples using nanomaterials including metal nanoparticles, carbon nanotubes and nanofilters. In spite of using a variety of nanomaterials to remove the residual of pharmaceuticals, there is still a dearth of successful applicability of them in industrial processes. Therefore, some defects of nanomaterials to be used for the removal of pharmaceutical contaminate in environmental samples and their impacts on human health and environment is briefly discussed.

Keywords: Hospital wastewater, Pharmaceutical, Nanomaterials, Wastewater, Nanoparticles, Carbon nanotube, Removal

INTRODUCTION

There is a wide range of both chemical and microbial contaminants that may be found in drinking-waters with adverse health effects on human being and the environment. Furthermore, the presence of pharmaceuticals or drug compounds in surface and ground water clearly represents an environmental challenge. This is particularly due to the unknown effects on human health and inadequate evidence of the impact on aquatic organisms. Understanding the sources of contaminations and how these may enter the water supply is critical for assuring water safety. Hospitals can act as main sources of pharmaceuticals input into the environment. Verlicchi and coworkers reported that characteristics of the hospital effluent is greatly dependent on the size of the hospital (the smaller hospital discharged

higher mean concentrations than the larger one), and season (concentrations tended to be higher in winter than in summer) [1]. Unfortunately, treatment of hospital wastewaters has become increasingly difficult due to the following major reasons:

- Hospitals discharge wastewaters containing chemicals and microbial agents into municipal wastewater treatment facilities [2,3]
- Many of the contaminants are resistant to normal wastewater treatment [4,5]
- Hospitals are the exclusive source of iodinated X-ray contrast media and other pathogens [4-6]

Referring to pharmaceuticals, large amounts of different compounds are used worldwide. Their sales have also been continuously increasing in the last decade. In particular, the annual consumption of sulphamethoxazole (an antibiotic) was equal to 22.4 t year⁻¹ in France, 47 t year⁻¹ in Germany and 12.7 t year⁻¹ in Spain. In the USA, approximately

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23,000 t of antibiotics is used each year [7]. Hospital wastewaters contains a complex mixture of active pharmaceutical ingredients and microorganisms. In most cases, these wastewaters are discharged to municipal wastewater treatment plants (WWTPs) without any pre-treatment [8]. Figure 2 shows some pharmaceuticals that are more commonly found in the environment according to their therapeutic activity. In each group, the most frequently detected pharmaceuticals are shown in bold [9,10].

The municipal WWTPs are not designed to remove persistent pharmaceuticals. In addition, the hazardous wastewaters may spread during flooding and combined sewer overflow events [2,4,8,9]. Due to the fact that environmental impact of trace levels of pharmaceuticals has not been clearly determined, there is an increasing focus on the potential environmental effects of pharmaceuticals in water environments. For example, Painkillers such as diclofenac and hormones have been shown to be capable of having fatal effects on fish, crustaceans and algae at very low doses [9,11-13]. Figure 1 shows pathways for the occurrence of pharmaceuticals in aqueous environment. To reduce the harmful effects of the mentioned pharmaceuticals, many wastewater treatment methodologies have been developed.

Traditionally, wastewater treatment methods have focused on removing pathogens, organic carbon, nitrogen and other nutrients that would otherwise enable harmful bacteria thrive and enter water courses [10,14]. However, previous reports reveal that small amounts of chemicals, including pharmaceutical compounds and endocrine disruptors are present in wastewater and remain even after treatment. The problem is that these micropollutants chemicals pose a danger to humans, aquatic organisms and their habitats [2,10,11,14].

As conventional water and wastewater treatment processes are unable to act as a reliable barrier toward some of recalcitrant pharmaceuticals, it is necessary to introduce additional advanced treatment technologies to recognize and anticipate persistent contaminants [15]. For this purpose, various treatment technologies have been evaluated in recent years including chemical oxidation using coagulation, ozone and ozone/hydrogen peroxide [16-19], biological treatment such as activated sludge process, membrane bioreactor (MBR), sequencing batch biological

reactor (SBR) process, membrane filtration such as reverse osmosis [20-24], and adsorption by activated carbon [19,20].

The ozone and ozone/hydrogen peroxide processes are highly energy and material intensive [25] and are only suitable for the treatment of relatively clean surface water and groundwater with less background contamination such as natural organic matter (NOM). The physical treatment processes also require the disposal of wastes such as membrane retentate and spent activated carbon generated during the treatment. In addition, activated carbon adsorption has a limited ability to remove polar organic compounds due to its removal mechanism (*i.e.*, hydrophobic interactions), especially in the presence of competitive NOM [26], while many pharmaceutical compounds and metabolites are indeed polar substances.

Nanotechnology, the deliberate manipulation of matter at size scales of less than 100 nm, holds the promise of creating new materials and devices which take advantage of unique phenomena realized at those length scales. These phenomena are due to their high reactivity which is caused by the large surface to volume ratio [27,28]. Application of nanomaterials for the removal of pharmaceuticals has come up as an interesting area of research [27,29]. They exhibit high adsorption efficiency especially due to high surface area and great active sites for interaction with various species. Furthermore, adsorbents with specific functional groups have been developed to improve the adsorption capacity of these materials [29].

The environmental fate and toxicity are critical issues to take into consideration in selection and design of different materials for water purification. Researches show that nanomaterials based methods include some advantages in comparison with other techniques used in water treatment. However, today the knowledge about the environmental fate, transport and toxicity of nanomaterials is still in infancy [27,30,31].

In this review, applications of nanomaterials are investigated for the removal of pharmaceuticals from hospital wastewaters. We provide an overview on some nanomaterial based techniques including metal nanoparticles, carbon nanotubes and nanofilters. Besides, some wastewater treatment methods by the mentioned materials are discussed briefly in the review.



Fig. 1. Pharmaceutical contamination routes of the aquatic environment.

SCOPE & OUTLOOK

The following sub-sections highlight applications of some nanomaterials in the removal of pharmaceutical in wastewaters [32,33]. The first sub-section (3.1) focuses on metal nanoparticles application for pharmaceutical removal from hospital wastewaters. It should be mentioned that iron oxide, titanium dioxide and some of their advance composites are explained in more detail. Sub-section 3.2 emphasizes on the introduction and application of carbon nanotubes and some of their composites in pharmaceutical

removal. In sub-section 3.3, we indicate that nanofiltration can be efficiently used as a removal membrane in pharmaceutical treatment.

OVERVIEW OF PHARMACEUTICAL REMOVAL BY NANOMATERIALS

Metal Nanoparticles

Nanoparticles have much larger surface areas compared to bulk particles on a mass basis. In addition, in order to enhance affinity of nanoparticles, they can be functionalized



Fig. 2. Most frequently detected pharmaceuticals in wastewaters and their concentrations.

with various chemical groups. Unique properties of nanoparticles have been employed to develop high capacity and selective sorbents for pharmaceutical removal. Characterizations of the nanoparticles are performed by transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM) and other instrumental techniques [5,28,31,32]. These nanomaterials can be used as photocatalysts or sorbents to degrade or adsorb the pharmaceuticals.

The advanced oxidation processes (AOPs) is one of the major procedures for the degradation of residual pharmaceuticals. This technique can provide almost total degradation. Many researches on the performance of AOPs for removing the residual pharmaceuticals are available [34–37]. The photocatalyst semiconductors such as TiO₂, ZnS, ZnO, CdS, Fe₂O₃ and *etc.* in photodegradation process are efficient metal nanoparticles for increasing the rate of degradation [38–40]. The high photocatalytic activity,

resistance to photocorrosion, low cost, non-toxicity, and favorable band gap energy are the advantages of a worthy suitable photocatalyst [38].

Among the various AOPs heterogeneous semiconductor photocatalysis, TiO₂ is widely used in recent years. This compound is capable of achieving complete oxidation of the water pollutants via hydroxyl radicals ([•]OH) and/or valence band (V_b) holes (h⁺) generated when the semiconductor is exposed to UV irradiation [34,41-44]. The photocatalytic reactions typically involve nanoparticle suspensions with the catalytic concentration being an important parameter that affects their efficient performance. Other parameters include light wavelength and intensity, pH of solution (which dictates the ionization state of the catalyst surface and consequently affects the extent of organics adsorption and degradation), the addition of H₂O₂ as an extra oxidant to promote reactions, and the water matrix [9].

In a study, photocatalytic degradation of meloxicam in the presence of TiO₂ nanoparticles has been studied for pharmaceutical wastewater treatment. Fractional factorial design was employed in order to investigate the effects of pH, irradiation time, UV light intensity, TiO₂ loading and initial meloxicam concentration on the efficiency of the process. The results showed that the light intensity is the most significant parameter followed by irradiation time and concentration, respectively. The optimum condition was applied for treatment of incurred water samples collected during various cleaning validation cycles. A percentage degradation of 77.34 ± 0.02% was achieved upon irradiation of samples containing 64.57 ± 0.09 µg ml⁻¹ with UV light in the presence of 0.4 mg ml⁻¹ TiO₂ nanoparticles at the pH 9.0 [31].

The high rate of recombination between photogenerated electron-hole pairs is a major rate-determining factor in determining the photocatalytic efficiency. This efficiency can be improved by depositing noble metals on their surfaces. The presence of metal atoms or clusters may help the electron-hole separation by trapping photoelectrons and thereby facilitating the photo-oxidation. Various metals including Pt, Pd, Ag, Au, Rh, *etc.* have been used for the enhancement of the photocatalytic activity of semiconductors. Among these metals, Ag is particularly suitable for industrial applications due to its availability and low cost [34,44-46].

The photocatalytic reactions usually follow the Langmuir-Hinshelwood kinetic model. This model is reduced to pseudo first or zero-order kinetics depending on the operating conditions [9]. From an engineering point of view, the use of catalyst in slurry form requires an additional treatment step to remove it from the treated effluent. To achieve the goal, it is suggested to use a combination between two process comprising photocatalysis and membrane separation process [9,47,48]. The membrane retains the used catalyst. In addition, the unreacted pharmaceuticals and their by-products separated by membrane can be recycled to the photoreactors [49-53]. The application of this technology is limited due to the fast recombination rate of photogenerated electron/hole pairs. According to recent researches, composite semiconductors could be an effective method, because they can increase the efficiency of charge separation and extend the energy range of photoexcitation [54,55].

In recent years, some reports indicated that introducing two or more proper elements onto nanocrystalline TiO₂ particles would improve the photocatalytic effect of TiO₂. Therefore, co-doping metal ions into the nondoped TiO₂ may have a synergetic effect to enhance the activity of TiO₂ [54,56,57]. The sol-gel process is suitable for producing composite materials of high purity without multiple steps [54,58]. Different methods such as photodeposition and impregnation have also been applied to prepare Ag/TiO₂ nanoparticles [34,59-61]. Nevertheless, there are a few numbers of studies concerning the photocatalytic degradation of pollutants using Ag/TiO₂ nanoparticles prepared by chemical reduction method [62]. Photocatalytic degradation of chloramphenicol and tartrazine was studied in the aqueous suspensions of silver-modified TiO₂ (Ag/TiO₂) nanoparticles under UV irradiation.

In addition, Sn/Zn/TiO₂ photocatalyst has been used for the oxidation of amoxicillin trihydrate (AMOX) as a target compound [54]. Metal co-doping was seen beneficial in terms of increasing the physicochemical specificities properties of TiO₂ such as specific surface area, crystallite size, pore volume, black light absorption. In addition, it prevented the anatase-to-rutile phase transformation. These were found favorable for the photocatalytic degradation of AMOX. More considerably, the higher activity of Sn/Zn/TiO₂ could be ascribed to the synergistic effect of

two doped metal ions with Sn, Zn functioning as electron traps and prevent the recombination of electron-hole pairs, consequently enhanced the charge separation [34].

In practical application, there is a problem that needs to be resolved for the TiO₂ photocatalyst. At present, although one-dimensional nanostructure TiO₂ can be fabricated by many methods [63,64], TiO₂ nanoparticles have a better application prospect for waste water treatment. However, when TiO₂ particles are dispersed into waste water, they are apt to be lost and difficult to be re-collected. To resolve this problem, photoactive TiO₂ particles are coated onto magnetic cores [63,65-68], and the coated particles can be re-collected by the action of a magnetic field. However, it is very difficult to achieve the complete coating at the nanometer level which needs the full dispersion of nano magnetic particles and the exact control of the surface electric charge of the TiO₂ particles. Usually, the composite photocatalyst is easier to be prepared compared to a coated photocatalyst. Furthermore, the magnetic cores which have remanence and coercive force are difficult to be separated again. However, the superparamagnetic materials, which have no remnant magnetism, can be re-collected and re-separated [68].

Treatment of pharmaceuticals in aqueous media by AOPs is likely to be an expensive venture. This is mainly because (i) extremely high conversions are needed (ideally below detection limit) as these compounds retain their adverse properties even at minute concentrations and (ii) initial concentrations are very low, thus making the treatment cost per unit mass excessive. A step in this direction is the use of renewable energy sources to power the processes as exemplified in the case of solar photocatalysis [9].

Besides the TiO₂, iron oxide nanoparticles are promising materials for industrial scale wastewater treatment, due to their low cost, strong adsorption capacity, easy separation and enhanced stability. Iron oxides exist in many forms in nature [69]. Magnetite (Fe₃O₄), maghemite (γ -Fe₂O₃) and hematite (α -Fe₂O₃) are the most common forms. The ability of iron oxide nanomaterials to remove contaminants has been demonstrated at both laboratory and field scale tests [69-71]. Current applications of iron oxide nanomaterials in contaminated water treatment can be divided into two groups: (a) technologies which use iron oxide nanomaterials

as a kind of nanosorbent or immobilization carrier for removal efficiency enhancement (referred to here as adsorptive/immobilization technologies), and (b) those which use iron oxide nanomaterials as photocatalysts to break down or to convert contaminants into a less toxic form (*i.e.* photocatalytic technologies). However, it should be noted that many technologies may utilize both processes. Additionally, iron oxide nanomaterials with low toxicity, chemical inertness and biocompatibility show a tremendous potential in combination with biotechnology [69,72].

In a research by Zhu *et al.*, iron oxide magnetic nanoparticles (Fe₃O₄ MNPs) were used to activate persulfate anions (S₂O₈²⁻) to produce sulfate free radicals (SO₄^{•-}), which are a powerful oxidant with promising applications to degrade organic contaminants. The kinetics of sulfamonomethoxine (SMM) degradation was studied in the system of Fe₃O₄ MNPs and S₂O₈²⁻. The authors reported a complete removal of the added SMM (0.06 mM) within 15 min with the addition of 1.20 mM S₂O₈²⁻ and 2.40 mM Fe₃O₄ MNPs. There was an optimum concentration of Fe₃O₄ MNPs because Fe₃O₄ MNPs may also act as a SO₄^{•-} scavenger at higher concentrations. Degradation mechanism of SUM on the basis of identification of the degradation intermediates was studied with liquid chromatography combined with mass spectroscopy [73].

In another work, Mackulak *et al.* reported the analysis of 27 selected psychoactive compounds found in the wastewater of the largest suburb in the eastern part of Central Europe Bratislava-Petržalka, Slovakia. Thirteen of them (MDMA, methamphetamine, amphetamine, THC-COOH, benzoylecgonine, codeine, tramadol, venlafaxine, oxazepam, citalopram, methadone, EDDP, cocaine) were found in concentrations above 30 ng l⁻¹. These compounds were selected for further monitoring. The possibility of complete degradation of these 13 substances by zerovalent iron and iron(VI) was studied in the wastewater from the Petržalka treatment plant. The degradation of synthetic drugs (methamphetamine, cocaine, MDMA) in wastewater was limited, while cannabis (of natural biological origin) is degraded with efficiency greater than 90%. After utilization of the Fenton reaction, its modification, and use of ferrate(VI), a high efficiency of eliminating all of these substances to values below the limit of detection was achieved [74].

In general, to assure their reactivity and mobility, nanomaterials should be stable to avoid aggregation and endow a low deposition rate. However, it is reported that nanomaterials tend to aggregate in solution. Commonly, the stability of colloidal nanoparticles is influenced by the electrostatic and van der Waals interactions. Much work is still needed to advance knowledge in the enhancement of nanomaterials stability by reducing their surface energy which limits their large-scale application. One attractive potential approach is the modification of nanomaterials based on the fact that some nanomaterials could react with various functional groups (for example iron oxide) to form stable materials [69-75].

Nanotubes

Since the discovery of carbon nanotubes (CNTs) in 1991, they have shown great potential in many medical and environmental remediation applications [76-78]. CNTs contain cylindrical graphite sheets, which have very high van der Waals index [76,79]. The benzenoid rings of graphite sheets have sp^2 -hybridized carbon atoms with high polarizability. These properties of CNTs make them superhydrophobic materials that may also strongly interact with aromatic pollutants through p-p coupling/stacking interactions [80,81]. These pollutants include nitroaromatics and amino- and hydroxyl-substituted aromatic compounds [82,83]. CNTs have various structures that are different in length, thickness, the type of helicity and number of layers. Although they are formed from essentially the same graphite sheet, their electrical characteristics differ depending on these variations, acting either as metals or as semiconductors [84]. As a group, CNTs typically have diameters ranging from <1 nm up to 50 nm. Their lengths are typically several microns, but recent advancements have made the nanotubes much longer, measured in centimeters [85].

CNTs can be categorized by their structures as [86]:

- Single-walled nanotubes (SWNT)
- Multi-walled nanotubes (MWNT)
- Double-walled nanotubes (DWNT)

Figure 3 presents a scheme that shows the nanostructure of a single-walled, double-walled and multi-walled carbon nanotube. Multi-walled carbon nanotubes are essentially concentric single walled tubes, where each individual tube

can have different chirality. These concentric nanotubes are held together by secondary and van der Waals bonding [87]. DWNT are a synthetic blend of both SWNT and MWNT, they exhibit the electrical and thermal stability of the latter and the flexibility of the former [86].

CNTs, owing to their large specific area, and high mechanical and chemical properties are considered as excellent candidates for wastewater treatment [86,88,89]. A CNT nano-structured sponge (nanosponge) containing sulfur and iron is more effective at soaking up water contaminants such as oil, fertilizers, pesticides and pharmaceuticals. Their magnetic properties also make them easier to be clean-up [86]. CNTs in particular received special attention for their exceptional water and wastewater treatment capabilities and proved to work effective against both chemical and biological contaminants [90]. In addition, CNTs are able to remove a wide range of contaminant heavy metals such as Cr^{3+} [91] Pb^{2+} [92], Zn^{2+} [93], metalloids such as arsenic compounds [94], organics such as polycyclic aromatic hydrocarbons (PAHs) [95-98] and a range of biological contaminants including bacteria [99-104], viruses [105,106], NOM [107-110] and cyanobacterial toxins [111-113]. The success of CNTs as an adsorbent media in the removal of biological contaminants, especially pathogens is mainly related to their unique physical, cytotoxic and surface functionalizing properties [90]. Some examples are summarized in the following:

The oxidized MWCNTs were used by Han *et al.* as adsorbents to investigate the effects of oxygen contents on adsorption properties of ciprofloxacin (CPX). With the oxygen content increasing from 2.0-5.9%, the normalized maximum adsorption capacity of CPX appeared growing state. However, the increment rate became slower, which is mainly attributed to p-p electron donor-acceptor interaction. The promotion of hydrophilicity and dispersibility, and the inhibition of water cluster had played a coordinate role in the whole adsorption process of CPX onto MWCNTs. Experiment data showed that CPX adsorption strongly depended on the pH of the solution. The alkaline condition was not conducive to the adsorption of CPX on MWCNTs. However, the ionic strength had no significant effect on the adsorption capacity of CPX onto MWCNTs. Therefore, the electrostatic interaction may be the main adsorption mechanism in the adsorption process [114].

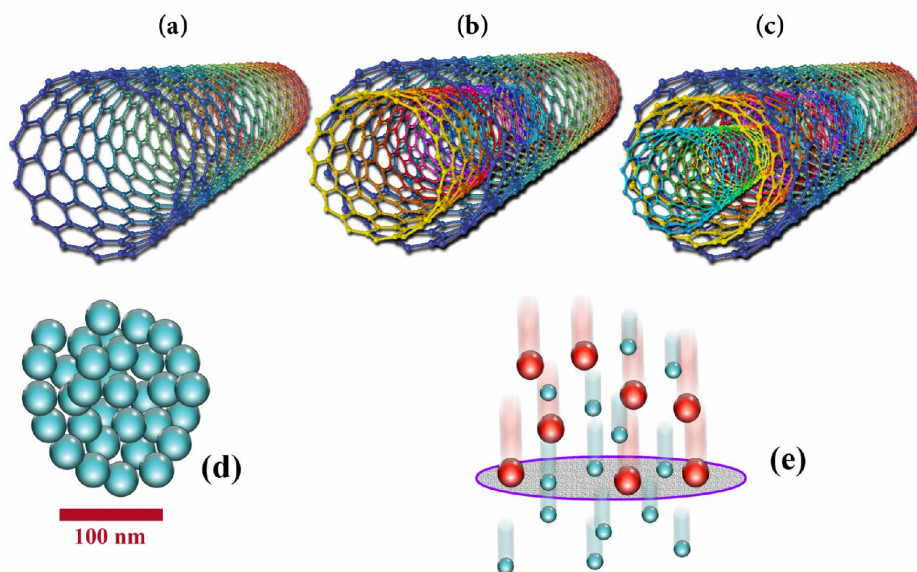


Fig. 3. Scheme of some nanomaterials a (a) single-walled carbon nanotube, (b) double-walled carbon nanotube, (c) multi-walled carbon nanotube, (d) nanoparticles and (e) nanofilter.

In an interesting work, Ahmad *et al.* produced a photo-regenerable multiwalled carbon nanotube membranes with variable water permeabilities by embedding hierarchical TiO_2 structures onto a pre-deposited bed of MWCNTs using a modified sol-gel technique. The adsorption removal potential of MWCNT/ TiO_2 membranes was demonstrated for three representative pharmaceuticals: acetaminophen, carbamazepine and ibuprofen. The peak initial removal percentages of the pharmaceuticals by the MWCNT/ TiO_2 membranes were 80%, 45% and 24% for carbamazepine, ibuprofen, and acetaminophen, respectively. The ability of the membranes to be regenerated once they were saturated with the pharmaceutical compounds was verified by repeating the adsorption removal experiment on the same membranes after exposure to UV light at 254 nm. Peak removal efficiencies after regeneration were 55%, 32% and 19% for carbamazepine, ibuprofen, and acetaminophen, respectively. This indicated some loss in sorption capacity upon regeneration [115].

In a different research, Czech *et al.*, developed a new MWCNT/ $\text{TiO}_2/\text{SiO}_2$ composite for the photocatalytic removal of bisphenol A (BPA) and carbamazepine (CBZ) from water solution. Nanocomposites with the addition of 0.15-17.8 wt% MWCNT show high potential for the

removal of both pollutants. The starting concentration of each contaminant was halved during 20 min of UV irradiation. The kinetics of the removal followed as a pseudo-first order regime with the k_1 in range 0.0827-0.1751 min^{-1} for BPA and 0.0131-0.0743 min^{-1} for CBZ [116].

It has been reported that various mechanisms simultaneously play roles in organic chemical adsorption such as hydrophobic, electrostatic, hydrogen bond, and π - π interactions. For example, if hydrogen bonds are predominant, CNT oxidation may increase organic chemical adsorption. However, if hydrophobic interaction is the overwhelming mechanism, CNT oxidation could decrease organic chemical adsorption. Thus, if the contributions of different mechanisms are unknown, an incorrect conclusion could be made in predicting the effects of CNT oxidation [117]. Fortunately, there are different functionalized CNTs available in the market such as hydrolyzed, carboxylate, and graphitized CNTs. Investigating the adsorption mechanisms on different types of CNTs can provide important information on understanding CNT-organic chemical interactions.

Various mechanisms may simultaneously control antibiotics adsorption on CNTs. Each adsorption

mechanism may be affected differently by environmental conditions. Therefore, it is of great importance to obtain the relative contribution of different mechanisms to the overall adsorption in the future [118]. Wider applications of CNTs have been facilitated by improvement in their production. In all carbon nanomaterials, cost has been the main limiting factor of commercialization. However, it is widely believed that if production scales increase, costs would decrease markedly. Moreover, in spite of high costs, using CNTs as adsorbents may be advantageous in future because the high adsorption capacities of CNTs compared to other media may offset their high cost. In addition, many researchers are branching out with the modification of CNTs by innovative processing techniques. However, there is still a considerable amount of room for enhancing CNT adsorption properties in future [118].

The main drawbacks of using CNT powders in water and wastewater treatment are the difficulties in handling and retrieving them through further filtration after the contaminant absorption. These issues can be addressed by using freestanding bulk CNT frameworks (mm sized), which are easy to handle [86]. CNTs are possibly one of the least biodegradable man-made materials ever devised. Once they are released into environmental compartments, one cannot exclude the possibility that CNTs may accumulate and their toxicity may biomagnify as they travel up food chains, due to their biopersistent and lipophilic nature [119]. CNTs may have significant impacts on the fate and transport of pharmaceuticals if they are released to the environment. Results presented today showed that CNTs may have potential risks for health of human beings. Therefore, characterization of CNTs and assessment of their effect on cells, organs, or the entire organism should also be standardized systematically so that nanotoxicity mechanisms can be uncovered and the safe use of CNTs can be achieved. Furthermore, the ecotoxicology of CNTs urgently needs to be studied, as it is essential for proper development of government regulations for the use of CNTs [119].

A better understanding of antibiotic/CNT interaction mechanisms and subsequent environmental behavior of both antibiotics and CNTs will provide a fundamental basis for the prediction of CNT risks. In addition, being aware of CNT risks would help to develop related guidelines for safe

design and application of CNTs [118]. CNTs have a high specific surface area, normally in the range of $290 \pm 170 \text{ m}^2 \text{ g}^{-1}$, and are generally lower than that of activated carbons (ACs) [120]. Carabineiro *et al.* and Wang *et al.* reported that antibiotics adsorption on ACs is higher than that on CNTs [84,121]. But, Peng *et al.* reported that ofloxacin (OFL) and norfloxacin (NOR) did not show the higher adsorption on ACs [85]. Single-walled CNTs showed comparable or even higher adsorption than ACs. The high specific surface area of ACs is attributed to its porous structure. It should be noted that N_2 molecules used in specific surface area measurement are much smaller than the OFL and NOR molecules. Thus, the N_2 -measured ACs surface may be not completely available for OFL and NOR adsorption. However, the specific surface area of CNTs is mostly its outer exposed surface and thus the availability of CNT surface would be higher than that of AC surface for OFL and NOR. Therefore, the specific surface area may not be a direct parameter to predict antibiotics/CNT interactions.

Four different models, the Freundlich model, Langmuir model, Polanyi-Mane model, and Dubinin-Ashtakhov model are often used to fit the adsorption isotherms. As different mechanisms including electrostatic interactions, hydrophobic interactions, π - π bonds, and hydrogen bonds, may act simultaneously, the prediction of organic chemical adsorption on CNTs is not straightforward [119].

Nanofilters

Nanofiltration (NF) is the most recent developed pressure driven membrane separation process and its applications have been increasing rapidly in the last decade. It has been widely used in aqueous systems such as the concentration of antibiotic aqueous solutions [123-127]. Removing hardness and dissolved organics from water [128-130], arsenic removal from drinking water [131], heavy metal ions recovery from electroplating wastewater [132] and separation of pharmaceuticals from fermentation broths [133] are some examples of industrial applications of nanofiltration. NF has characteristics that lie between ultrafiltration (UF) and reverse osmosis (RO). In general, RO membranes reject both organic matters and salts [130,134] while UF membranes freely pass all salts and most organic matters.

NF membranes, on the other hand, retain matters that

can penetrate UF membranes, except some low molecular weight micropollutants that can be rejected by RO membranes. Moreover, NF membranes retain bivalent ions but still are relatively permeable for monovalent ions [135]. Since all NF membranes have their origins in RO membranes, they are called loose RO membranes or tight UF with respect to its permeate flux and separation performance [136]. These kinds of membranes have originally served as an attractive economic alternative to RO membranes due to the lower operating pressures involved and higher water permeability.

The nominal molecular weight cut off (MWCO) of NF membranes is in the range of 100-1000 Da [137,138]. Therefore, the molecular weight of antibiotics is coincident with the range of MWCO of NF membranes and the noticeable difference in molecular weight between AMOX and other materials in the wastewater makes it possible for them to be separated effectively with NF membranes [137]. There are many studies on the application of nanofiltration for removal of pharmaceutical compounds from waste waters. In most studies, the percentage removal obtained for different membrane types was higher than 90% for all the pharmaceutical (antibiotic classes) studied [139-142]. Koyuncu *et al.* obtained the lowest values for the removal of tetracyclines (50-80%) and sulphonamides (11-20%) [143].

Naproxen, a non-steroidal anti-inflammatory drug, commonly used for fever, inflammation and different health problems has been recently detected in sewage effluents, surface and ground water, and sometimes even in drinking water. A WWTP utilizing UF, AC and RO after the primary biological treatment by Karaman *et al.*, showed that both nano- and micro-ultrafiltration were not sufficient for removing spiked naproxen to a safe level, whereas RO membrane was quite efficient [144]. No naproxen degradation was detected in pure water whereas it underwent biodegradation within three days in activated sludge giving *O*-desmethyl-naproxen. Adsorption process performed on micelle-clay complex and AC under steady state conditions indicate that the former adsorbent is highly effective in removing naproxen with fast kinetics. Laboratory micelle-clay complex filters under continuous naproxen-spiked water flowing were found to be efficient in removing this drug, suggesting that the efficiency of

existing advanced WWTP could be improved by including filtration columns filled with suitable sand/micelle-clay mixtures.

In a research, Zárny *et al.* offered a new possible way for the removal of persistent organic pollutants. In their study, cyclodextrin containing nanofilters having different chemical composition and thickness (1.5-3.5 mm) were investigated. For their characterization, their adsorption capacity was determined applying ibuprofen containing model solution and total organic carbon analyzer. It could be established that the regeneration of nanofilters with ethanol and the application of inorganic additives (NaCl, NaHCO₃, NH₄HCO₃) increased the adsorption capacity of nanofilters. The best results were achieved with chemical composition of 30 m/m% β -cyclodextrin polymer beads and 70 m/m% ultra-high molecular weight polyethylene in the presence of 12 mmol ammonium hydrogen carbonate/nanofilter [145].

Similar to adsorption, these techniques produce a new solid residue (membrane), where the contaminant is concentrated. So far, these techniques have been mostly used in combination with other methodologies. NF is a temperature sensitive processes (this parameter significantly affects feed pump pressure, the hydraulic flux balance between stages and solubility of the dissolved salts in the effluent), organic material occurring naturally in the water matrices and the concentration of the dissolved salts. The presence of high concentration levels of these compounds can cause membrane structure deterioration or fouling [138].

CONCLUSION AND FUTURE WORK

This review has addressed some advances in pharmaceutical removal from hospital wastewaters from the standpoint of using nanomaterials including metal nanoparticles, carbon nanotube and nanofilters. Pharmaceuticals such as antibiotics and anti-inflammatory drugs which are designed to be biologically active substances, have the potential for accumulation and persistence in the environment. They may have the adverse health effects on human being and the environment. Various treatment technologies have been reported including chemical oxidation using coagulation, ozone and

Table 1. Summary of the Removal/Degradation Processes Applied in Treatment of Pharmaceuticals Using Nanomaterials

Applied process	Pharmaceutical	Operating conditions	Summary of results	Ref.
<i>Nanoparticles</i>				
TiO ₂ /UV (photocatalytic oxidation)	Chloramphenicol and tartrazine	Room temperature with pH of about 6.5, I ₀ = 50 W m ⁻² , [Pollutant] ₀ = 20 mg l ⁻¹ , [Catalyst] = 400 mg l ⁻¹ .	Above 84 and 89% mineralization of CAP and TAZ was observed using 120 min irradiation.	[34]
ZnS	β-lactam antibiotics	ZnS (0.1 g l ⁻¹) β-lactam antibiotics (500 mg l ⁻¹); pH 4.5 and time of 60 min.	The optimized conditions for degradation of β-lactam antibiotics are pH 4.5 and 0.5 mg l ⁻¹ of catalyst. The degradation rate of β-lactam antibiotics is in order of: CLX > PEG > PEV > AMP > AMO	[38]
Sn/Zn/TiO ₂	AMOX	[Sn/Zn/TiO ₂]: 400 mg l ⁻¹ , [AMOX]: 20 mg l ⁻¹ , T: 296 K, pH 5.6.	Less energy is consumed during the degradation of AMOX in the presence of Sn/Zn/TiO ₂ compared with other photocatalysts.	[54]
TiO ₂ /UV, TiO ₂ /H ₂ O ₂ /UV and Fe ²⁺ /H ₂ O ₂ /UV	Trimethoprim and sulfamethoxazole	TiO ₂ /UV at pH = 6; TiO ₂ /H ₂ O ₂ /UV at pH 4.5 and 7; Fe ²⁺ /H ₂ O ₂ /UV at pH = 2.8 and with 5 mg Fe ²⁺ /l	Heterogeneous photocatalysis, combining TiO ₂ and H ₂ O ₂ an effective solution for the degradation of sulfametaxazole and trimethoprim antibiotic solutions under natural solar conditions and mineralization rates were substantially lower when compared with the photo- Fenton reaction.	[122]
TiO ₂ /SiO ₂ /Fe ₃ O ₄	Diclofenac	1.0 × 10 ⁻³ M diclofenac in 0.1 M Na ₂ SO ₄ , pH = 10	The magnetically attached TSF electrode showed higher PEC degradation efficiency with desirable stability. Such a TSF loaded electrode was applied to PEC degradation of diclofenac. After 45 min PEC treatment, 95.3% of diclofenac was degraded on the magnetically attached TSF electrode.	[146]

Table 1. Continued

<i>CNTs</i>				
MWNTs and MWNTs-COOH	2-nitrophenol	at 25 °C; initial 2-nitrophenol concentrations: 45 mg l ⁻¹ , 85 mg l ⁻¹ , 130 mg l ⁻¹ , 160 mg l ⁻¹ , 310 mg l ⁻¹ . pH at 4-11	While pH exceeded 8 there was a fall in the uptake of 2-nitrophenol. The Langmuir isotherm model better explained the adsorption isotherms as compared to the Freundlich model.	[147]
AC, CNT and carbon xerogel	CPX	100 mg l ⁻¹ CPX, pH = 5	The carbon nanotubes sample presents the best performance per unit surface area.	[84]
SWCNT and MWCNT and powdered AC	Iopromide, lincomycine and sulfamethoxazole	SWCNTs (purity > 95%, length 1-5 μm, and outer diameter 1.5 nm) and MWCNTs (purity > 95%, length 1-5 μm, and outer diameter 15 ± 5 nm), three pharmaceuticals (concentration: 12,000 mg l ⁻¹)	The adsorption generally followed the order SWCNT > PAC > MWCNT. The relatively low adsorption on MWCNT was probably due to its lower specific surface area than other carbon materials.	[76]
Hydroxylized, carboxylized, graphitized MWCNTs and SWCNTs	CPX	pH at 7, CPX concentration = 35 mg l ⁻¹	Desorption of antibiotics from CNTs may lead to potential exposure, particularly under changing environmental conditions such as temperature and pH. The irreversibility of desorption hysteresis (TII) followed the order of SW > MH > MG > MC.	[148]
MWCNTs	OFL and NOR	The pH adjusted to 7.0 ± 0.2 OFL (700 mg l ⁻¹) and NOR (60 mg l ⁻¹)	site-specific adsorption was not important but hydrophobic effect may have an important contribution to OFL and NOR adsorption on CNTs.	[85]
Graphitized MWCNTs, Carboxylated MWCNTs, hydroxylated MWCNTs, and AC	Norfloxacin	To compare the pH effect, single concentration point sorption experiments were conducted at different pHs using initial concentrations between 25 and 26 mg l ⁻¹ at 298 K. initial concentrations (10-40 mg l ⁻¹)	In the range of pH < 7.2, <i>K</i> of NOR increased with increasing pH, while at pH > 7.2, <i>K</i> declined with increasing pH.	[121]
Hydroxylized, carboxylized, and graphitized MWCNTs	Sulfamethoxazole	pH at 2-12, initial concentrations 50 mg l ⁻¹ .	At pH around 3.7, SMX always showed the highest adsorption on different CNTs and the adsorption followed the order of MH > MG > MC.	[117]

Table 1. Continued

<i>NF</i>	
NF and Ro	<p>Bezafibrate, bisoprolol, carbamazepine, clarithromycin, CPX, diclofenac, ibuprofen, metronidazole, moxifloxacin, telmisartan, tramadol</p> <p>MBR pre-treatment. the pump pressure was only 7 bar for the NF and 14 bar for RO.</p> <p>Comparing the tested NF and RO-only (a two stage) RO is appropriate to remove pharmaceutical residues from hospital wastewater entirely.</p> <p>[149]</p>
NF membrane	<p>AMOX</p> <p>COD and AMOX concentrations in the membrane feed were 24225 mg l⁻¹ and 1825 mg l⁻¹, respectively. Pressure ranged from 3-15 bar. pH at 6.</p> <p>The rejection of the AMOX by the selected NF membrane was adequate and in most cases exceeded 97% whereas COD reached a maximum of 40% rejection and permeation flux was over 1.5 l min⁻¹ m⁻².</p> <p>[137]</p>
Combined NF and mild solar photo-Fenton	<p>Carbamazepine, flumequine, ibuprofen, ofloxacin, sulfamethoxazole</p> <p>Pharmaceuticals (15-150 g l⁻¹), mild solar photo-Fenton operated at pH 5-6, low iron (5 mg Fe²⁺/l) and hydrogen peroxide concentrations (<25 mg l⁻¹).</p> <p>Concentration of five pharmaceuticals at 15 g l⁻¹ by NF produced a permeate containing less than 1.5% of the initial concentration of pharmaceuticals and a concentrated stream containing around 150 g l⁻¹ of each compound. Solar photo-Fenton process applied to this stream led to a reduction of 88% and 89% in treatment time and hydrogen peroxide consumption, Respectively</p> <p>[150]</p>
NF combined with advanced tertiary treatments solar (photo-Fenton, photo-Fenton-like Fe(III)-EDDS complex and ozonation)	<p>carbamazepine, flumequine, ibuprofen, ofloxacin, sulfamethoxazole</p> <p>concentrations of 15, 60 and 150 g l⁻¹ of each pharmaceutical for final concentrations of 75 g l⁻¹ (15 g l⁻¹ of each pharmaceutical) to 300 g l⁻¹ (60 g l⁻¹ of each), pH was around 8-8.5</p> <p>General advantages of the combined process over direct treatment due to reduction in the total volume to be treated were: (i) lower AOP treatment time, (ii) more efficient reagent consumption, and (iii) lower acid consumption for carbonate removal.</p> <p>[151]</p>
NF combined with ozone-based advanced oxidation processes	<p>NOR, OFL, roxithromycin, azithromycin</p> <p>Water recovery of 75% during NF. Four antibiotics spiked at 600 g l⁻¹ for each analyte with pH of 7.9.</p> <p>High rejections of antibiotics (>98%) were obtained in all sets of NF experiments.</p> <p>[152]</p>

ozone/hydrogen peroxide, biological treatment such as activated sludge process, membrane bioreactor, sequencing batch biological reactor process, membrane filtration such as ROs, and adsorption by AC in recent years. Much progress has been made over the last few years to develop applications of nanomaterials in this field. These nanomaterials can help us to obtain suitable methods to destroy or remove the pharmaceuticals from wastewater samples. These applications of nanomaterial are originated from their high adsorption efficiency due to high surface area and great active sites for interaction with various species including pharmaceuticals. In addition, the surface modification to enhance the dispersion property of nanomaterials in solution can greatly increase the interaction of nanomaterials with pollutants, and thereby increase their removal capacity. An overview of the published papers in scientific journals between 2010-2014 years has been presented in Table 1. However, some limitations on their application for removal of pharmaceutical must be taken into consideration:

Firstly, the aggregation of nanomaterials in aqueous solution, limits the available sites for binding with pollutants. Secondly, using nanomaterials in water and wastewater treatment are the difficulties in handling and retrieving them through further filtration after the contaminant absorption (CNT as an example). Thirdly, they may have significant effects on the fate and transport of pharmaceuticals if they are released to the environment.

Ultracentrifugation separation method is efficient in separating nanomaterials. However, high energy is necessary in this method. Membrane filtration method is another efficient technique to separate nanomaterials from aqueous solutions. However, the membrane may be easily blocked. Compared with centrifugation and filtration methods, the magnetic separation method is considered a rapid and effective technique for separating nanoparticles from aqueous solution.

Generally, the above methods have some advantages and disadvantages. However, to select the best method and material for wastewater treatment, a number of factors must be considered such as the quality standards which have to be met and the efficiency as well as the cost. Also, these conditions must be considered in the decision on wastewater treatment technologies: (1) treatment flexibility and final

efficiency, (2) reuse of treatment agents, (3) environmental security and friendliness and (4) low cost.

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