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Nanostructured Aerogel Materials for removal of Antibiotic from Contaminated Environment: A Review

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ABSTRACT:

Antibiotics are commonly using for killing of human and animal host pathogenic fungi and bacteria. It was reported that annual global consumption of antibiotics is ranging between 100 hundred thousand to 200 hundred thousand tones. Therefore, the aquatic system is carrying such kind of toxicants and consequent severe impact on human health and other biotic components in the ecosystem. Therefore, water system containing antibiotics is gained to attention of decontamination by appropriate technology. The adsorption process is a popular technique having easy operation, economically convenient, wide selectivity, significant efficiency for decontamination of antibiotics. Among other adsorbents, the aerogels are reported as low cost with excellent properties including high porosity, low density, extended surface area (108–539 $m^2 g^{-1}$), biocompatibility and biodegradability etc. The aimed of this review was to evaluate the modification routes, adsorption efficiency and mechanistic insight of adsorption mechanisms of antibiotics were explored by reported studies.

Keywords: Nanostructured, Aerogel, Antibiotic, Removal, Adsorption, Wastewater, Environment;

Introduction:

Rapid increasing rate of population growth and subsequent amassed demands of modernizationandcomfort, healthy and quality life of human being is prompts to rising pollutants including antibiotics in our environment [1-5]. Concurrently, demanded huge rate of pharmaceuticals (antibiotic, analgesics and hormones), pesticides and drugs are producing and subsequently discharging of intractable toxicants into the environment is prompts to rising of pollutants of environment including water [6-8]. The emerging pharmaceuticals (EPs) including antibiotic and analgesics are considered in the top priority list of pollutants by the European Union (EU) and the United States Environmental Protection Agency (US EPA) for the determination of water quality based on them. The complex mixture of toxins by EPs in the water system is gained to immediate attention of decontamination by appropriate technology. Apart from other wastewater treatment technologies, the adsorption is considered as promising, low-cost and one of the easiest methods for wastewater decontamination [9,10]. Thetype of contaminants and concentration of pollutants in the wastewater are varied based on human induced activities at different geographical location of the world[11,12].For example, acomprehensive research in the 100 European rivers of 27 EU countries were found that some antibiotics were frequently detected with high concentration that including carbamazepine, benzotriazole and caffeine in the all water bodies of surveyed European rivers [8,9]. Several studies in Germany have been reported that the level of pharmaceuticals including antibiotics were detected more than 80% in the water treatment sites. Among other pharmaceuticals products, the antibiotic such as sulfamethoxazole and roxithromycin were found at concentration of 6 µg/L [8]. On the other hand, some studies were reported in the United Kingdom that the clotrimazole was detected with concertation at 22 ng/L in the rivers of Tees, Mersey, Tyne and Thames [8]. The both industrial effluents and inland water samples were analyzed and pharmaceuticals pollutants were detected at range of 11-695 and 4-2370 ng/L, respectively. Other study was found that the antibiotic propranolol was detected in the sites of wastewater treatment plants (WWTPs) in England [13]. In corollary, several studies were conducted across the world for detection of ECs for instance the concentrations at ranging of 0.01-0.06 µg/L of naproxen and diclofenac was detected in the drinking of Brazil [8]. The 139 streams around 30 states of USA were studied the concentration of antibiotics and reported that mostly the ulfamethoxazole with concentration of 490 ng/L, carbamazepine with concentration of 420 ng/L and atrazine with concentration of 130 ng/L were found in the drinking water from the aquifer [8,9]. A comparative study was reported that the antibiotics including sulfamethazine, sulfamethoxazole and trimethoprim was detected with concentration at the range of 7-360 ng/L in the River Tamagawan of Japan and 4-448ng/L in the Mekong Delta of Vietnam. The previous study was found that the ciprofloxacin was detected in the samples of WWTPs of Hyderabad India with high concentration at 31mg/L due to effect of pharmaceutical industrial effluents [8]. The groundwater, inland water even portable water was detected of antibiotics with concentrations of mg/L values. In the River Mankyung of South Korea was found some antibiotics including clarithromycin with concentration of 443 ng/L, fluconazole at 111 ng/L carbamazepine at 595 ng/L and ibuprofen with concentration at 414 ng/L. In the Pearl River Delta in South China was detected some antibiotics including ibuprofen with concentration of 1417 ng/L. The effect of these antibiotics on human health is lead to reduce the immunity and some of them are carcinogenic [13]. Even some time they can acts as malfunctions agents of hormones and subsequent alarming disorder in the human body. Hence, wastewater with antibiotics should be decontamination by appropriate technology. Usually,the mostly applying treatment process for the removal of antibiotics are liquid–liquid extraction, membrane separation, photocatalysis, adsorption, electrocoagulation, ozonation etc [13-23]. The adsorption process is a popular technique having easy operation, economically convenient and most efficient for antibiotics sequestration [1-5]. Apart from other used adsorbents, the nanostructured aerogel materials are considering as good alternatives candidates for the decontamination of wastewater due to the excellent properties of aerogels including porous structured, extremely light materials along with extended specific surface area, easily measureable and easy to separation and regeneration from the solution [14].This review mainly exemplifiesthe modification process of nanostructured aerogels and subsequent application of nanostructured aerogels for antibiotics adsorption. Adsorption efficiency and mechanistic insight of adsorption mechanisms were explored by recent reported works on antibiotics adoptions onto nanostructured aerogels.

Types of Aerogels and Their Advancement

Based on forms and appearance of aerogels they can be films, powders and monoliths etc. Aerogels can be typed as nano-aerogels, hybrids, polymers, oxides and composites in accordance of chemical structured and synthesis routes. Based ondraying methods of aerogels also denoted as cryogels, aerogels and xerogels etc. The most useful classification of aerogels is organic, inorganic and composite/hybrid aerogels, every types also being further categorized based on the nature of used pristine for gel formation of aerogels. Samuel Stephens Kistler in 1931 was invented the aerogel [14]. From the beginning of invention, different types of aerogels are chronologically fabricating and customizing to outfit of pollutants considering with cost and efficiency of applications. The end of last century in 1996, firstly synthesized the activated carbon using organic polymers by the activation of CO_2, and it was found excellent adsorption capacity. Then, aerogels have been developed with combination of various precursors. At the beginning of this century, the scientific community have been continued synthesis of nanostructured aerogels and they wereexhibitedas high electrical thermal and conductivity, excited mechanical strength and extended surface area and higher efficiency of removal of pollutants [14]. The nano-aerogels having 2-50 nm of pore diameter are extremely low weighted and highly porous materials. Moreover, functionalization of nano-aerogels is can easily coupling with diverse adaptable functional groups to crafting abundant of functionalities for enhancing adsorption capacity [12-14].

Nanostructured aerogels:Nanomaterialsdenoted as between 1-100 nm of size of nanoparticles [5]. Nanostructured aerogels are thegreatest alternative adsorbents due to their excellent physical and chemical surface properties and wide range of selectivity of pollutants [14]. Nanostructured aerogels aretolerating and manufacturing of building blocks with other single adsorbents in a nano-size range and subsequently formed of different nanostructured aerogels [14]. The modification and combination of pristine aerogels with other functional adsorbents can enormously enhance the adsorption capacity due to presence of multifunctional properties including abundant binding sites in the functionally tailored aerogel. Nanostructured aerogels were reported as modified with different materials including polymers, inorganic carbon, metal oxides and silica as illustrated in the Fig-1 [14].

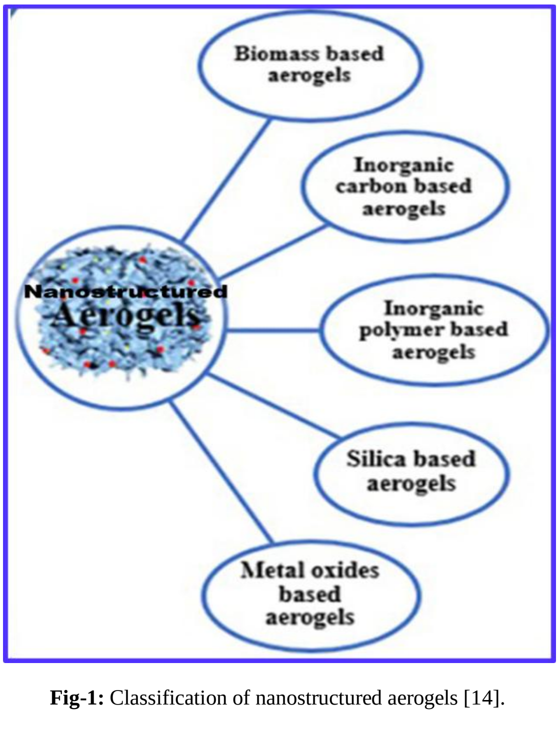

Fig-1: Classification of nanostructured aerogels [14].

Modification Routes of Nanostructured Aerogels:

The modification routes of aerogels are mainly three steps including hydrolysis, gelation and drying. The hydrolysis is the first step where modification aerogels start with mixing of precursors in the solution either water or organic solution after that gelation is the process of gels formation by catalytic or crosslinking agents and finally releasing liquid portion from the pores of materials by draying as seen in Fig-2 [12]. The formation of hydrogel is an intermediate product of aerogel synthesis, several methods are following for the formation of this intermediate product(hydrogel) of aerogel that including sol-gel, hydrothermal, self-assembling, molecular and colloidal approach, template synthesis and chemical vapor deposition etc.[14].

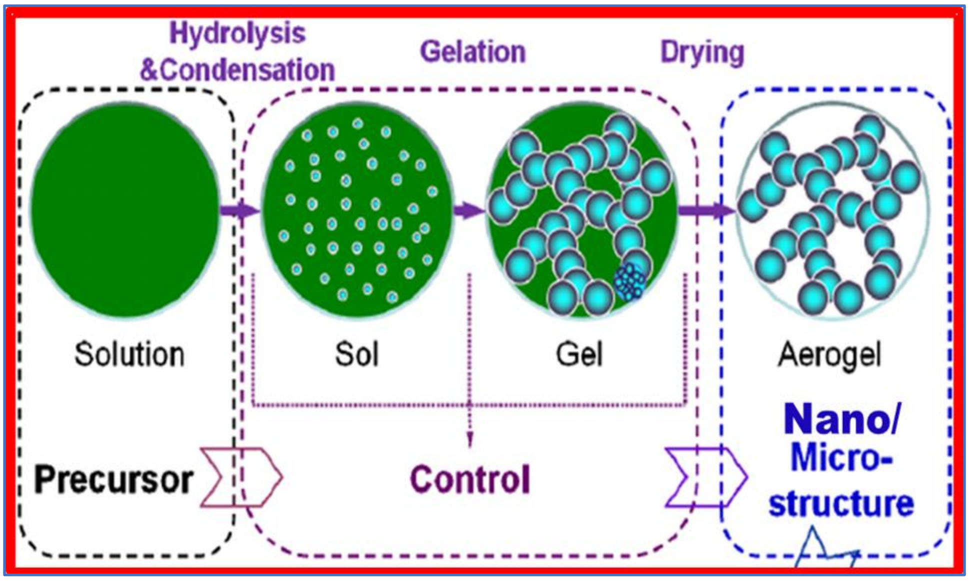

Fig-2: Key steps of aerogelmodification [12].

Methods of hydrogel formation afore aerogel preparation:Several methods are applying for the formation of hydrogel before modification of aerogels including self-assembly method, sol–gel method, hydrothermal method etc.Sol-gel is a traditional and widelyapplied process for hydrogel formation and it's a process of hydrolysis and condensation of precursors and subsequent formation a crisscross network of hydrogels. In the sol gel process, low temperature is required and hydrolysis reaction can easily control and be able to precisely develop customized nanostructured gel [8-14]. The three key steps are roughly use for this sol-gel process including gelation, aging and drying as seen in Fig-2 [12]. On the other hand, the hydrothermal method refers to hydro-chemical process for hydrogel formation, this method also one of the popular method of fabrication of intermediate product of aerogels. The water is applying as solvent media within airtight sealed vessel with high pressure and temperature. The ultimate hydrogels were rapidly formed without altering the integrity and structure of materials.Other prominent hydrogel formation method is the self-assembling which is one of thecost effective methods for hydrogels formation.

Methods of drying for aerogel preparation:The success of modification of aerogels is depending on drying method as because of extraction of liquid part from hydrogels is most critical and challenging step. Drying is one of the fundamental and vital steps for the preparation of aerogel from wet-gel platforms. Aerogels, xerogels and cryogels are common light gel materials were denoted based on the drying methods in the fabrication process. Associated elements including power, energy carbon dioxide etc. are required in the different drying processes which is concern to environmental degradation. Some commonly drying processes are using to protecting the brittleness/fragileness of the aerogels. These are mainly freeze drying (FD), ambient pressure drying (APD) and supercritical drying (SCD) [14]. Apart from others, the FD are most effective for the preparation of aerogels, it is highly motivated drying process in the scientific community due to low energy consumption and subsequent environmental benefit[14]. APD having some limitation such including time consuming and extra cost required for chemical and reagents at large scale production. The SCD method is frequently involves in highly tight autoclave environment with high cost, while the FD offers widely industrial applications of aerogels fabrication due to cost and environmental sustainability.

Nanostructured aerogels for removal of antibiotics:

The aerogels are considering as worthymaterials for removal of antibiotics due to their exciting surface properties including low density, excellent thermal conductivity, extremely light materials along with extended specific surface area and easy to separation from the solution. The previous studies were widely reported that aerogel materials can be use several times, so regeneration facility also one of the attractions on aerogels for the decontamination wastewater with antibiotics [14]. Last few decades have observed pronounced modification advancement of aerogels that including incorporation of metal oxides, polymers, silica, carbon and biomass etc. The fabrication and modifications were customized to outfit of pollutants nature for better adsorption efficiency. Some of studied aerogels materials are summarized in Table-1 along with their removal capacity of antibiotics. Apart from other aerogels, the nanostructured bio-aerogels were reported as good super adsorbents for the removal of antibiotics. Bio-aerogels can be withstanding at high compression as well as can be possible up to 80% plastic deformation without collapse of pore wall. Among other bio-aerogels, cellulose based aerogels are reported as low cost with excellent properties including high porosity, low density, extended surface area (108–539 m^2 g^{-1}), biocompatibility and biodegradability etc. But single cellulose-based aerogels are owning only OH (hydroxyl) radicals and they are obviously low adsorption capacity in comparison of other functional groups like carboxyl, amino etc. [14].

Table-1: Some aerogels and their capacity of antibiotic removal

Sl	**Nanostructured aerogels**	**Adsorption capacity (mg/g)**	**Adsorption conditions**		**Reusability (Cycles)**	**Refs.**
			pH	Time(min)		
1	CNC-PVAm/rGO	Sodium diclofenac 605.87	7	60	4	[24]
2	Aamphiphilic cellulose aerogel (HCNC-TPB/TMC)	Sodium diclofenac 526.32	4-10	60	6	[24]
3	Chitosan/activated biochar (CS-ABC2)	Ketoprofen 188	4.0	90		[25]
4	Functional cellulose aerogel (Cell@PEI)	Sodium diclofenac 294.12	5.0	180	5	[26]
5	Chitosan–aerogel–activated carbon (CHT:AEO:AC)	Naproxen 0.147 /99%	7.0	372.5	4	[27]

A nanocrystaline cellulosic aerogel (CNC-PVAm/rGO) was modified with reduced graphene oxide using polyvinylamine (PVAm) and subsequently applied to decontamination of diclofenac sodium (DCF). The highly porous structure and extremely light CNC-PVAm/rGO was found an excellent adsorption capacity (605.87 mg/g) of DCF even 53 times higher than the pristine cellulose (11.45 mg/g) due to –OH and $–NH_2$ functional groups, extended surface area (105.73 m^2/g). DCF removal onto CNC-PVAm/rGO was endured as spontaneous exothermic and best fitted to the models as pseudo-second-order kinetic and the Langmuir isotherm. At least 4 times of recycling could be possible [24]. Chen et al., [25] was evaluated the novel fabricated aerogel named CS-ABC2 for the decontamination of ketoprofen (KTP). KTP is mainly using an anti-inflammatory drug and it is a carcinogenic and toxic. The adsorption of KTP onto CS-ABC2 was good with regeneration facility. This bio-aerogel was fabricated applying non-template process using 10% of ABC in the CS subsequent enhancement of mechanical strength. The aerogel was exhibited environment friendly, low cost, biodegradable and easy to separation from solution.An aerogel was cross-linked with cellulose in Polyetherimide (PEI) named as Cell@PEI, and the aerogels were applied for the decontamination DCF. The monolayer adsorption was 294.12 mg/g with 5 times of reusing facility. The abundant function groups and extended surface area (241.41 m^2/g) were promoted the adsorption rate through synergetic actions of hydrogen bonding and electrostatic attraction between DCF molecules and the surface of functional Cell@PEI [26].Ozcan et al., [27] was utilized a chitosan-based bio-aerogel fabricated by incorporation of activated carbon for removal of naproxen from wastewater. The aerogel was good adsorbent with 90 % of removal capacity and 4 successive regenerations. Spontaneous exothermal energetic reactions were followed and adsorption process was best conformed to the Langmuir isotherm and pseudo-second-order kinetic model.

Adsorption mechanisms of antibiotics onto nanostructured aerogels:

Adsorption mechanism of antibiotics onto functional aerogels were proposed by several reported studies that are mainly hydrogen bonding, electrostatic interaction, π-π stacking, and hydrophobic interactions etc. (Fig-3) [28]. Generally, molecular structures of antibiotics such as Oxytetracycline (OTC), cefoxitin sodium and diclofenac sodium (DCF) are combination of carboxyl, chlorine, imine and benzene groups. The antibiotics with available carboxyl group in water contact is negative, so that positively charge aerogels is may propose the electrostatic interaction between the anionic antibiotic and cationic aerogel, while aerometric benzene ring may also propose the hydrophobic interactions and π-π stacking which is offer the subsequent adsorption promotion [14,28].

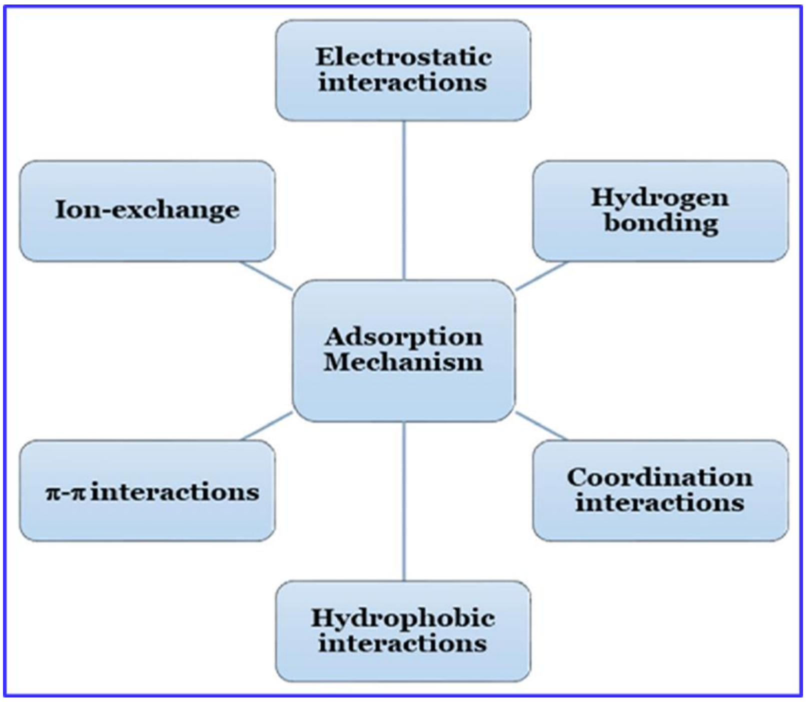

Fig-3: Common adsorption mechanisms of antibiotics removal onto aerogels [28].

Conclusion:

In this review, the reported studies were summarized and the aerogel materials are considered as good alternatives candidates for the decontamination of antibiotics due to the excellent surface properties including porous structured, extremely light materials along with extended specific surface area and easy to separation and regeneration from the solution.The pristine aerogels having insufficient radicals and low adsorption rate in comparison of tailored/coupled aerogels with other functional groups like carboxyl, amino etc. Drying is one of the fundamental and vital steps for the preparation of aerogel from wet-gel platforms. Associated elements including power, energy carbon dioxide etc. are required in the different drying processes which is concern to environmental degradation. Apart from others, the FD are most effective for the preparation of aerogels, it is highly motivated drying process in the scientific community due to low energy consumption and subsequent environmental benefit. The adsorption mechanisms of antibiotics are mainly hydrogen bonding, electrostatic interaction, π-π stacking, and hydrophobic interactions etc by active participation of carboxyl, chlorine, imine and benzene groups available in the antibiotics. Therefore, nanostructured aerogels are promising nano-adsorbent for water purification and ultimate environmental remediation.

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