



Nanosponge cyclodextrin polyurethanes and their modification with nanomaterials for the removal of pollutants from waste water: A review



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ABSTRACT

Water is a worldwide vital resource for sustaining life and due to the pollution of water by different classes of pollutants (inorganic, organic and pathogens), many ongoing studies in water purification remain a critical issue to governments, scientists and industries. The challenge is to develop a water purification technology which will be effective at removing these contaminants simultaneously and reducing their concentrations to ultra low levels from waste water. This review article serves to give an overview on cyclodextrin nanosponge adsorbents which have already been used for water treatment. The modification of these cyclodextrin nanosponges with existing adsorbent nanomaterials (carbon nanotubes, TiO₂ and silver nanoparticles) and the factors affecting the adsorption capacity of these nanosorbents are discussed. The nanotoxicity of these engineered nanosorbents material is also addressed since nanotoxicity is a major concern to human health and environment.

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1. Introduction

Water is essential in many aspects of human life such as health, food, economy and energy. Nowadays, the access to safe drinking water around the world and especially in South Africa has been limited, due to population growth, climate change and environmental water pollution by sewages, industrial effluents, chemicals, domestic wastes and pesticides, etc. (Amin, Alazba, & Manzoor, 2014; Mhlanga, Mamba, Krause, & Malefetse, 2007).

In this regard, water purification and sanitation have now become the main critical issue world-wide. The removal of pollutants present in industrial wastewater, surface and/or ground water, is currently the major concern because even when not toxic, they can produce bad colour, odour and taste problems (Amin et al., 2014; Mhlanga et al., 2007). At very low levels, inorganic pollutants such as heavy metals (e.g. cobalt, lead, chromium), and organic compounds (e.g. polychlorinated, endocrine disrupting compounds (EDC), natural organic matter (NOM)) are still very toxic and harmful to human health (Mhlanga et al., 2007; Sithole, Mamba, Krause, & Mapolie, n.d.). Moreover, microorganism contaminants such as pathogens (e.g. bacteria, viruses, protozoan parasites) are also source of various health issues (waterborne diseases) (Dungeni, van Der Merwe, & Momba, 2010).

Nowadays, the removal of pollutants to ultra-low levels still remains a big challenge. Many conventional water treatment techniques such as ion exchange, molecular sieves, coagulation, sedimentation-flocculation, reverse osmosis, ozonation, chlorination, membrane filtration absorption processes, chemical precipitation, electrochemical techniques, have been employed to resolve the issue (Dungeni et al., 2010; Fu & Wang, 2011; Gunatilake, 2015; Nxumalo, 2006). However there are some limitations presented by these techniques since they are sometimes associated with problems such as their high costs, their incapability to successfully remove contaminants from water to the satisfactory levels and the sludge generated (Gunatilake, 2015; Ihsanullah et al., 2016). Table 1 summarises the advantages and disadvantages of some of these techniques. Moreover these techniques are specific for either inorganic pollutants (with also reference to heavy metals) or organic pollutants but organic, inorganic and pathogenic microorganism contaminants coexist in the waste water environment (Mamba, Mbianda, Govender, Mamba, & Krause, 2010). Currently, these techniques are now facing the challenges posed by new emerging pollutants. (Amin et al., 2014; Sithole et al., n.d.).

In order to solve the limitations presented by the above conventional remediation techniques, the nanotechnology adsorption processes were developed (Bora & Dutta, 2014; Dungeni et al., 2010; Qu, Alvarez, & Li, 2013). This is because of their simplicity, their low cost and their high efficiency. They are also not a source of waste generation which means they can be regenerated by an appropriate desorption process (Amin et al., 2014; Dungeni et al., 2010; Ihsanullah et al., 2016). The use of nanotechnology in adsorption processes requires the use of nanoadsorbent materials (Qu et al., 2013). Hence, this paper gives an overview of the type of nanosorbents which have been used for waste water treatment by focussing on the nanosponge cyclodextrins insoluble polymer and their chemical modifications with carbon nanotubes, titanium dioxide and silver nanoparticles. The factors affecting the adsorption mechanisms and challenges on the environmental safety of these nanosorbent materials and future research recommendations are also mentioned.

2. Adsorbent nanomaterials used for water purification

Adsorbent nanomaterials also called nanosorbents, are nanostructured materials with pore size between 1 and 100 nm onto which the pollutant molecules can be adsorbed (Amin et al., 2014; Bora & Dutta, 2014; Chorawala, 2015). They are also classified as nanoporous materials. The nanosorbents to be reviewed in this article include the nanosponge cyclodextrins, carbon nanotubes and metal nanoparticles (e.g. TiO₂ and Ag).

Other common types of conventional adsorbent materials which have already been used for water purification are the zeolites (Chibban, Zerbet, Carja, & Sinan, 2012; Crini, 2006; Mohan & Pittman, 2006), clays (Ali, Asim, & Khan, 2012; Crini, 2006), chitosan (Chibban et al., 2012; Crini, 2006), activated carbon (Ali et al., 2012; Chibban et al., 2012; Crini, 2006; Mohan & Pittman, 2006), silica beads (Crini, 2006), agricultural solid wastes (e.g. rice husk) (Ali et al., 2012; Crini, 2006) and industrial by products (e.g. fly ash, peat chars) (Ali et al., 2012; Crini, 2006). Table 2 presents the advantages and limitations of some of these conventional adsorbents.

Previous reports have demonstrated that the efficiency of conventional adsorbents was limited by their poor adsorption kinetics, lack of selectivity, low surface area, and poor regeneration (Ali et al., 2012; Chibban et al., 2012; Crini, 2006; Chorawala, 2015; Mohan & Pittman, 2006).

Nanosponge cyclodextrin polyurethanes (nanoporous insoluble polymers), on the other hand have proven to be good adsorbents for the removal of organic contaminants including dyes (Crini, 2003), fertilizers and pesticide (Background Paper for the International Workshop on Nanotechnology, Water & Overview, n.d.; Mamba, Krause, Malefetse, Gericke, & Sithole, 2008; Mamba, Krause, Malefetse, & Nxumalo, 2007; Rima & Assaker, 2013; Wang, Wang, Zhou, Han, & Lü, 2014). Previous studies have demonstrated that cyclodextrin polymers were able to remove pollutants to parts-per-trillion whereas zeolites and activated carbon were able removed to parts-per-million (Background Paper for the International Workshop on Nanotechnology, Water & Overview, n.d.). However previous literatures have demonstrated that it is very difficult to specify clearly which one among the different types of adsorbent materials is the best (Ali et al., 2012; Crini, 2006). This is because of the inconsistencies in data presentation; the adsorption capacity and efficiency obtained for each type of adsorbents depends on the conditions of the experiments and the method used for water treatment (column, reactors or batch method) (Crini, 2006). In addition, each type of adsorbent material has its own specific properties, advantages and disadvantages in waste water purification (Crini, 2006).

Hence one can only modify the existing adsorbent materials in order to improve their properties and adsorption capacity toward different kind of water pollutants (Krause, Mamba, Bambo, & Malefetse, 2010; Lukhele, Krause, & Mamba, n.d.; Salipira, 2007). For instance, this study reports on the synthesis and used of the nanoporous insoluble polymers (nanosponge cyclodextrin polyurethanes) in water treatment as well as their modification with nanomaterials.

2.1. Cyclodextrins and their application in water treatment

Cyclodextrins (CDs) were first reported in 1891 by A. Villiers (Villiers, 1891). They are cyclic oligosaccharides, synthesized by enzymatic reactions of starch with the amylase of *Bacillus mac-*

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