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NANOMATERIALS USED IN TREATMENT OF WASTEWATER: A REVIEW

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Abstract: Water pollution affect environment and human health so we have varied methods to fight it. One of the advanced method is nanotehnology. Traditional techniques are generally effective (extraction, adsorption and chemical oxidation), but often very expensive. It is very important to be able to reduce toxic levels of pollutants in an efficient way, at reasonable cost. That is why intensive research is being done on nanotechnologies. Great improvements have been made using nanotechnology for resolving water pollution problems, in the future it will have better advantages. Nanotechnology is an eco-friendly treatment that gives us a very efficient and durable approache. This paperwork presents the difference between traditional methods of wastewater treatment and nanotechnology. The advantages of using nanomaterials are highlighted in relation to the environmental impact, implementation costs and performance of those nanomaterials.
Keywords: wastewater treatment, nanotechonoly, carbon nanotubes

1. INTRODUCTION

One of the major problem that we are facing today is water pollution. Water pollution affect environment and human health so we have varied methods to fight it. One of the advanced method is nanotehnology because nanoparticles have very high absorption capabilities and can act in depth and any location. With a very small size, nanomaterials (NMs) can achieve energy conservation that can lead to cost savings (Deepa Madathil et al., 2013).
Traditional techniques are generally effective (extraction, adsorption and chemical oxidation), but often very expensive. It is very important to be able to reduce toxic levels of pollutants in an efficient way, at reasonable cost. That is why intensive research is being done on nanotechnologies (Fact sheet, 2009). Since the use of nanoparticles in water treatment requires high technology, the cost of using this method should be depending on the competition existing on the market (Crane et al., 2012). Research has been done using different nanomaterials (nanosorbent, nanocatalyst, bioactive nanoparticles, biomimetic membrane and molecular polymers MIPs) to remove toxic metal ions, organic and inorganic solvents from water.

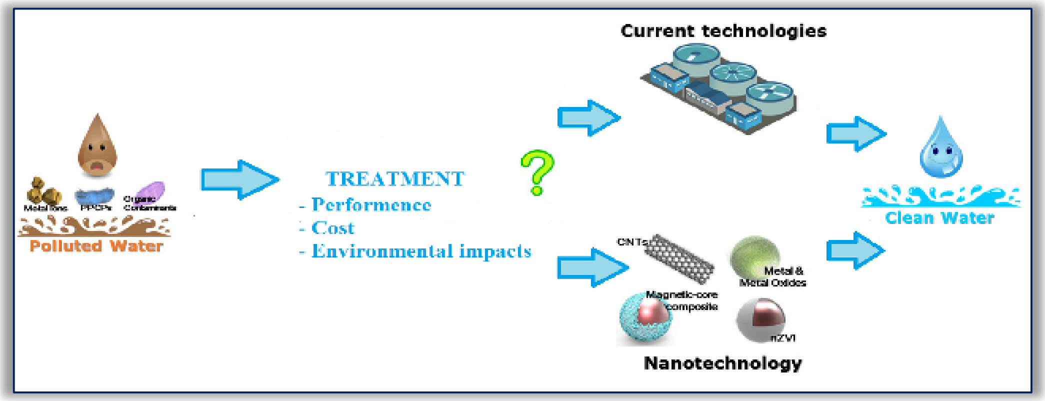

Figure 1 - Current technologies or nanotechnology application for water treatment (Adeyemi S et al., 2016)

Nanotechnology is applied to treat wastewater to detect and remove various pollutants. By applying various methods such as photocatalysis, nanofiltration, adsorption and electrochemical oxidation using TiO_2, ZnO, ceramic membranes, nanowire membranes, polymer membranes, carbon nanotubes, metal oxides, magnetic nanoparticles, water quality problems are reduced (Karisma et al., 2015). Nanotechnology promises an immense improvement in manufacturing technologies, electronics, telecommunications, health and even environmental remediation (Gross, 2001; Kim et al., 2005; Moore, 2006). It requires the production and usage of a vaste range of NMs, including structures and devices that have the size ranging from 1 to 100 nm and presents unique properties not found in traditional method materials (Stone et al., 2010; Wang et al., 2010). Several types of nanomaterials, such as carbon nanotubes (Mauter and Elimelech, 2008; Upadhyayula et al., 2009) and TiO_2 NMs (Khan et al., 2002; Shankar et al., 2009), have been hard studied and very reviewed.
Nanoadsorbents have a high affinity for adsorption of substances. Having properties such as high porosity, small size and active surface, nanoadsorbents have the ability to retain pollutants with variable molecular size, hydrophobicity and speculation behavior (S. Pacheco et al., 2006). Nanoadsorbents have the advantage of working fast, have pollutant binding capabilities and can be chemically regenerated after exhaustion (K. Yang et al., 2007).

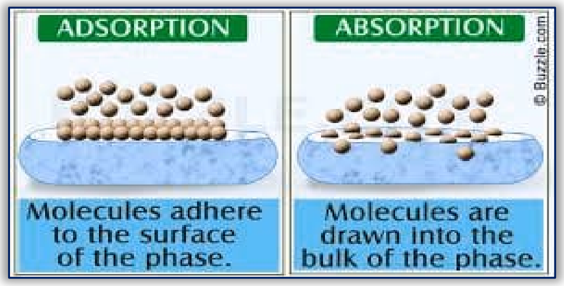

Figure 2 - Difference between adsorption and absorption (H.O.D Dr.Komal Mehta et al., 2018)

2. MATERIALS AND METHODS

— Zeolites

One of the oldest and important wastewater treatment is the use of natural zeolites in the areas of their application. A major environmental problem is the appearance of heavy metals (Zn, Cr, Pb, Cd, Cu, Mn, Fe, etc.) in wastewater and their disposal by natural zeolites have been extremly studied side by side with other technologies. The main methods for heavy metals removal are chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation flocculation, flotation and electrochemical methods (Fu F *et al.,* 2011). Nowadays, many studies are set on investigating natural zeolites as adsorbents in wastewater treatment and their properties. Multiple natural zeolites worldwide have shown good ion-exchange capacities for cations, such as ammonium and heavy metal ions. These natural zeolites can be modified by performing several methods, such as acid treatment, ion exchange, and surfactant functionalization. Those zeolites that were modifed showed high adsorption capacity also for organic matter and anions (Wang S *et al.,* 2010).

— Properties of natural zeolites

Natural zeolites have complex and interesting structure. SiO_4 and AlO_4 tetrahedra are the primary building units (PBU) of zeolites. They connect via oxygen ions into secondary building units (SBU), which are then linked into a three-dimensional crystalline structure of zeolite. Si can be substitute by Al which defines the negative charge of the zeolite framework, which is compensated by alkaline and earth alkaline metal cations. Natural zeolites that have negative charge on the surface appear as cation exchangers. In the zeolite lattice, substitution is not limited to Si-Al substitution. Atoms of iron, boron, chromium, germanium, and titanium also can substitute silicon. We can find water molecules in voids of large cavities and chained to framework ions and exchangeable ions through aqueous ties. Clinoptilolite is the most researched zeolite in basic and applied studies. The fact that these materials are very porous with channels and cavities, that have characteristic pore sizes and shapes, represents the characteristic way of binding of PBUs and the formation of unique structural units. In the clinoptilolite structure are three types of channels, two are parallel, made of ten and eight-membered rings of Si/AlO_4, meanwhile the third one is vertical and defined by eight-membered rings. In these channels the places that the hydrated cations can occupy are: I - cation (Na- and Ca-ions) is situated in the 10-member ring channels (free diameters 0.44 x 0.72 nm); II - cation (Na- and Ca-ions) is situated in the 8-member ring channels (free diameters 0.41 x 0.47 nm); III - cation (K- ion) is situated in the 8-member ring vertical channels (free diameters 0.40 x 0.55 nm); IV - cation (Mg-ion) is situated in the channel of 10- member rings and it is situated in the center of the channel (Figure 3).

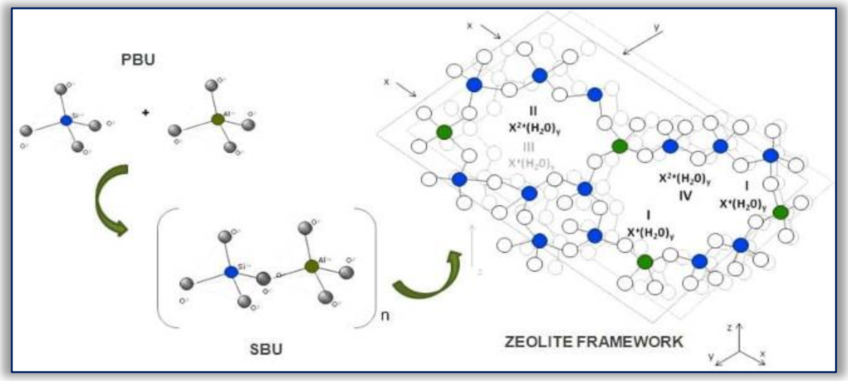

Figure 3 - Primary building units PBU and secondary building units SBU in three-dimensional zeolite- clinoptilolite structure (Karmen Margeta et al.)

3. RESULTS

The high adsorption capacity and thermal stability is represented by carbon-based adsorbents including carbon, carbon nanotubes, fullerenes and graphene (C. Santhosh et al., 2016). From all the various adsorbing nanomaterials, carbon has been investigated as a superior adsorbent for the elimination of inorganic and organic pollutants. When carbon nanotubes (CNT) and fullerenes were discovered, these materials were widely used as effective adsorbents (K. Yang et al., 2006). Carbon nanotubes are composed of a cylindrical shape wrapped in a tube. Carbon nanotubes are two types, single-wall carbon nanotubes (SWCNTs) and multi-wall carbon nanotubes (MWCNTs), where single-wall carbon nanotubes are composed of a single sheet of rolled graphene, and multi-wall carbon nanotubes are composed of several sheets of rolled graphene. Figure 4 shows the

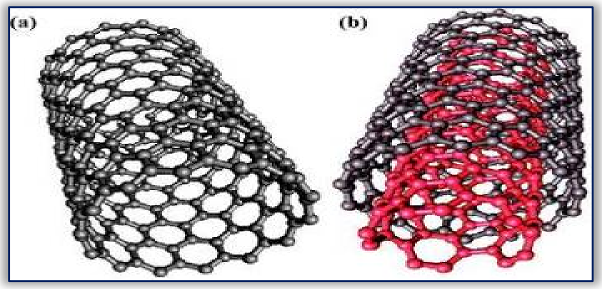

Figure 4 - Structures of SWCNTs (a) and MWCNTs (b) (C. Santhosh et al., 2016)

structures of SWCNTs (a) and MWCNTs (b) (C. Santhosh et al., 2016). Carbon nanotubes have an exceptional adsorption capacity and high efficiency compared to the conventional method of using activated carbon (X. Wang *et al.,* 2008).

— Nanocatalysts

Due to their special characteristics, nanocatalysts are also very used in wastewater treatment because it enhances the catalytic activity at the surface. It increases the reactivity of contaminants. Semiconductor materials are the most used catalytic nanomaterials (zero-valence metal and bimetallic nanoparticles) for degradation of environmental contaminants such as PCBs (polychlorinated biphenyls), azo dyes, halogenated aliphatic, organochlorine pesticides, halogenated herbicides, and nitro aromatics (Xin et al., 2011). The catalytic activity has been showed in the laboratory for different pollutants.

— Nanostructured catalytic membranes (NCMs)

Nanostructured catalytic membranes are commonly used for wastewater treatment. It has several advantages such as high uniformity of catalytic sites, capability of optimization, limiting contact time of catalyst, allowing sequential reactions and ease in industrial scale up (Deepa Madathil *et al.,* 2013).

— Bioactive nanoparticles

Water contamination is the main reason for lots of infectious diseases due to various contaminating pathogens. Many of the microorganisms acting as pathogens are highly resistant to antibiotics and this make them very hard to remove them from water. Recently the concept of bioactive nanoparticles has emerged which has given the alternative of new chlorine – free biocides (Deepa Madathil *et al.,* 2013).

— Biomimetic membrane for water treatment

Biomimetic membranes are a new and advanced way for wastewater treatment because of its specific design and fabrication. This method uses self-assembly and atomic layer deposition tuned nanopores which basically gives highflux desalination. Through this method impurities like salt and others are removed from water with applied pressure powered by electrical energy (Deepa Madathil *et al.,* 2013).

— Molecularly imprinted polymers (Mips)

Molecularly imprinted polymers is a new method that has emerged as one of very fine ways for various biological, pharmaceutical and environmental applications. The high selectivity of the polymers is due to its synthetic procedure where a template molecule is linked to suitable monomer(s) having functional groups by covalent, semi covalent or non-covalent bonds providing subsequent specific binding sites to the MIPs. The left imprint after the removal of template from polymer helps in recognizing properties of the MIP and are generally called binding sites (Deepa Madathil *et al.,* 2013).

4. CONCLUSIONS

Great improvements have been made using nanotechnology for resolving water pollution problems, in the future it will have better advantages. Nanotechnology is an eco-friendly treatment that gives us a very efficient and durable approach. These methods are cheaper, less consuming for both time and energy and it has less waste generation than traditional based methods. Due to the usage of nanoparticles certain measures must be taken for human health and safety and for the environment.

Using nanomaterials should be easy implemented, cost effective and friendly. Mass commercialization of nanosorbents will be applied after 10 years of research. Certain criteria such as technical, economic and social challenges have to be defined for the success of good commercialization of nanomaterials.

The appearance of heavy metal ions and dyes in wastewater is a major problem for environment and human health. The disposal method of these ions has not reached the perfect conditions. Natural zeolites have been very studied, due to their unique properties, for heavy metals and dye disposal from wastewater because of their high surface area, low particles size which leads to high numbers of adsorption active centres.

Zeolites have their adsorption properties, high porosity and excellent thermal stability that makes them very appropriate for most applications, also in wastewater treatment. Many studies have showed that they are very good in removing the contaminants (heavy metals, anions and organic matter) from wastewater. Because of their surface binding of biological agents from water modified natural zeolites are more and more used for biological treatment of wastewater. Future studies can be focused on the improvement of the surface modification methods to increase their efficiency and to enlarge the capability of regeneration. Furthermore, detailed characterization of natural and modified zeolites is needed to better understand the structure-property relationship.

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References

[1] Adeyemi S. Adeleye, Jon R. Conway, Kendra Garner, Yuxiong Huang, Yiming Su, Arturo A. Keller, Engineered nanomaterials for water treatment and remediation: Costs, benefits, and applicability, Chemical Engineering Journal, 286 (2016) 640–662;
[2] Chella Santhosh, Venugopal Velmurugan, George Jacob, Soon Kwuan Jeong, Andrews Nirmala Grace, Amit Bhatnagar, Role of nanomaterials in water treatment application: a review, Chemical Engineering Journal 306, 2016, 1116-1137;
[3] Crane R. A., Scott T. B., Nanoscale zero-valent iron: Future prospects for an emerging water treatment technology. J Hazard Mater, 2012, pp 211-212.
[4] Fact sheet, Emerging Contaminants – Nanomaterials, Solid Waste and Emergency Response (5106P),EPA 505-F-09-011, United States Environmental Protection Agency September 2009;
[5] Fu F, Wang Q, Removal of heavy metal ions from wastewaters: A review. J.Environ.Manage., 2011, 92:407-418;
[6] G.P. Rao, C. Lu, F. Su, Sorption of divalent metal ions from aqueous solution by carbon nanotubes: a review, Sep. Purif. Technol. 58, 2007, 224–231;
[7] Gross M. Travels to the nanoworld: miniature machinery in nature and technology. New York: Plenum Trade, 2001;
[8] H.O.D Dr.Komal Mehta, Prachi Sata, AdityaSaraswat, Devanshu Mehta, Nano materials in water purification, International Journal of Advance Engineering and Research Development, Conference of Nanotechnology & Applications In Civil Engineering-2018;
[9] Karishma K. Chorawala, Mehali J. Mehta, Applications of Nanotehnology in Wastewater Treatment, International Journal of Innovative and Emerging Research in Engineering, 2015;
[10] Karmen Margeta, Nataša Zabukovec Logar, Mario Šiljeg and Anamarija Farkaš, Natural Zeolites in Water Treatment – How Effective is Their Use;
[11] Khan SUM, Al-Shahry M, Ingler WB., Efficient photochemical water splitting by a chemically modified n-TiO2. Science; 2002, 297(5590):2243;
[12] Kim D, El-Shall H, Dennis D, Morey T., Interaction of PLGA nanoparticles with human blood constituents. Colloids Surf B; 2005, 40(2):83–91;
[13] K. Yang, L. Zhu, B. Xing, Adsorption of polycyclic aromatic hydrocarbons by carbon nanomaterials, Environ. Sci. Technol. 40 (2006) 1855–1861;
[14] K. Yang, B. Xing, Desorption of polycyclic aromatic hydrocarbons from carbon nanomaterials in water, Environ. Pollut. 145, 2007, 529–537;
[15] Mauter, M.S., Elimelech, M., Environmental applications of carbon-based nanomaterials. Environmental Science and Technology 42 (16), 5843e5859, 2008;
[16] M.B. Seymour, C. Su, Y. Gao, Y. Lu, Y. Li, Characterization of carbon nanoonions for heavy metal ion remediation, J. Nanopart. Res. 14, 2012, 1–13;
[17] Moore MN., Do nanoparticles present ecotoxicological risks for the health of the aquatic environment? Environ Int;32(8), 2006, 967–76;
[18] N. Invernizzi, G. Foladori, E. Robles-Belmont, E. Záyago Lau, E. Arteaga Figueroa, C. Bagattolli, et al., Nanotecnologías dirigidas a necesidades sociales. Contribuciones de la investigación latinoamericana en medicina, energía y agua, Sociol. Technosci. 5 (2) (2015) 1–30;
[19] Pan, B., Xing, B.S. Adsorption mechanisms of organic chemicals on carbon nanotubes. Environmental Science and Technology 42 (24), 2008, 9005e9013;
[20] Prachi, Pranjali Gautam, Deepa Madathil, A. N. Brijesh Nair, Nanotechnology in Waste Water Treatment, International Journal of ChemTech Research, 2013;
[21] Shankar K, Basham JI, Allam NK, Varghese OK, Mor GK, Feng XJ, et al. Recent advances in the use of TiO2 nanotube and nanowire arrays for oxidative. J Phys Chem C; 2009, 113:6327–59;
[22] Shah, M.A., Ahmed, T. Principles of Nanoscience and Nanotechnology. Narosa Publishing House: New Delhi, India, pp. 34-47, 2011;

[23] S. Pacheco, M. Medina, F. Valencia, J. Tapia, Removal of inorganic mercury from polluted water using structured nanoparticles, J. Environ. Eng. 132, 2006, 342–349;
[24] Stone V, Nowack B, Baun A, van den Brink N, von der Kammer F, Dusinska M, et al., Nanomaterials for environmental studies: classification, reference material issues, and strategies for physico-chemical characterisation. Sci Total Environ; 2010, 408(7): 1745–54;
[25] S. Wang, C.W. Ng, W. Wang, Q. Li, L. Li, A Comparative study on the adsorption of acid and reactive dyes on multiwall carbon nanotubes in single and binary dye systems, J. Chem. Eng. Data 57, 2012, 1563–1569;
[26] Upadhyayula VKK, Deng S, Mitchell MC, Smith GB. Application of carbon nanotube technology for removal of contaminants in drinking water: a review. Sci Total Environ 2009;408(1):1-13;
[27] Wang LB, MaW, Xu LG, Chen W, Zhu YY, Xu CL, et al, Nanoparticle-based environmental sensors. Mater Sci Eng R; 2010, 70(3–6):265–74;
[28] Wang S, Peng Y, Natural zeolites as effective adsorbents in water and wastewater treatment. Chem. Engin.J., 2010, 156:11-24;
[29] X. Ren, C. Chen, M. Nagatsu, X. Wang, Carbon nanotubes as adsorbents in environmental pollution management: a review, Chem. Eng. J. 170, 2011, 395–410;
[30] X. Wang, J. Lu, B. Xing, Sorption of organic contaminants by carbon nanotubes: influence of adsorbed organic matter, Environ. Sci. Technol. 42, 2008, 3207–3212;
[31] Xin Zhaoa,b, Lu Lva,b, Bingcai Pana,b, Weiming Zhanga,b, Shujuan Zhanga, Quanxing Zhanga,b., Polymer-supported nanocomposites for environmental application: A review, Chemical Engineering Journal, 170(2–3), 2011, pp 381–394;
[32] Y. Gao, Y. Li, L. Zhang, H. Huang, J. Hu, S.M. Shah, X. Su, Adsorption and removal of tetracycline antibiotics from aqueous solution by graphene oxide, J. Colloid Interface Sci. 368 (2012) 540–546.

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