DENITRIFICATION OF GROUNDWATER USING GRAPHENE, GRAPHENE OXIDE AND NANOCOMPOSITES

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Abstract

Pollution of air, soil and water is a global concern for the human society and their environment. Removal of these pollutants from the environment is a huge challenge. Compared to other techniques adsorption techniques are more effective and simple in the removal of contaminants and depend on their pore and surface properties. New size based physiochemical properties formulate nanoparticles with huge range of applications in biomedical, sensors, electronic devices catalyst, membranes removing environmental pollutants and so on. New carbonaceous nanomaterials graphene and graphene oxide which has large high surface area and functional groups signifying their prospective for the adsorption processes. In this review paper, we highlight few current advances in graphene and graphene oxide nanocomposites for the removal of nitrate from water. Nanocomposites material enhances adsorption capacity as well separation efficiency by modifying graphene or else graphene oxide. To increase the adsorption rate by activation of graphene and graphene oxide using nanocomposites will be a promising way for further research in denitrification of groundwater.

Keywords: *Graphene, Graphene oxide, Nanocomposites*

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1. INTRODUCTION

Nitrogen, an essential element, forms an integral component in living organism in its molecular or ionic forms and its biological mediated pathways include symbiotic fixation, plant uptake, ammonification, immobilization of nitrate, nitrification, denitrification, leaching and through volatization into the atmosphere as ammonia, nitrous oxide and gaseous nitrogen (Archna *et al* 2012). Industrialization, growing food and energy demand have lead to anthropogenic emissions of nitrogen compounds at alarming rates ever than before. The nitrogen spread through water and air as a resultant of excessive use of fertilizers, domestic water lechates, municipal waste treatment plant effluents have entered ground water aquifers (Anderson *et a*l 2014, Loganathan *et al* 2012, Shrimali *et al* 2001).

Prominent levels of nitrate in potable water can cause many health problems like stomach cancer, methehemoglobinemia (blue baby syndrome), diabetes, other infectious diseases in humans. Conversion of nitrate to nitrite, causes serious health risk by reacting with hemoglobin to cause (cyanosis) bluish discoloration of the skin in newborn infants due to inadequate oxygenation of the blood (Archna *et al* 2012).

In cattle's, and some other domestic animals acute poisoning can take place within 4hours after ingestion of plants or high concentration of nitrate through water. According to EPA and WHO guidelines, the maximum allowable nitrate concentration is 50mg/L by nitrate and 10mg/L by nitrogen, accepted as safe for public water system (Fataei *et al* 2014).

Recently, using nanotechnology some important pollutants like nitrate are being removed from water resources (Roco *et al* 2010) .Use of nanofilters is the newest method to treat and eliminate water pollutants (Bhattacharya *et al* 2013) and are known to have a higher potential in converting nitrate to nitrite (Fataei *et al* 2014, Sharma *et al* 2009).

Graphene is a miraculous, the world's first two-dimensional (2D) material and latest addition to the carbon family that has attracted attention. Graphene, hottest nano-material in nanotechnology has fascinated the scientific research community by its diverse novel properties (Geim *et al* 2008). Graphene symbolize, a theoretically novel class of material that is only one atom thick with 2D layer of hybridized sp^2 carbon, offers novel inroads into research that has never ceased to astonish and continues to offer a fertile ground for applications (Huang *et al* 2012).

Several properties of graphene like chemical, mechanical and electronic make it functional for fabricating nanocomposites materials. Being 200 times stronger than steel, tensile strength of the nanocomposites material can be increased by doping metals and plastics by graphene (Novoselov *et al* 2004, 2012).

2. REMOVAL OF WATER POLLUTANTS USING NANOTECHNOLOGY

Recently, availability of clean water is a major issue and it is quite difficult to solve due to the associated problems. Only 30% of total volume of water available on earth is available for human consumption. The other 70% are trapped in the glaciers or is in the form of ice and out of the available 30%, only 0.08% of it is completely clean (Krantzberg *et al* 2010, Wang *et al* 2013). Groundwater, surface water and waste water are polluted by various sources such as waste disposed, leaked fertilizers, herbicides, oil spills, by-products of processes and combustion, pesticides, fossil fuels extraction etc.(Sharma *et al* 2009, Liu *et al* 2012).

To remove these dissolved impurities, various processes such as reverse osmosis, ultra filtration, nano filtration, solar desalination etc have been used and they have shown high adsorption capacity in removal of some of the important pollutants like organic compounds, heavy metal cations and anions (Upadhyayula *et al* 2009, Foo *et al* 2010). These advanced methods use of nano-materials made of activated carbon, carbon tubes , graphene and graphene oxide carbon nanotubes, biopolymers, single-enzyme nanoparticles, self assembled monolayer on mesoporous support system, zeolites, nanoparticles of zero valent iron are used for water remediation (Liu et al 2012) with enhanced affinity, capacity, selectivity for heavy metals and other contaminants. Higher reactivity, larger surface contact and better disposal capability are the advantages of using nanomaterials in the removal of water pollutants (Wang *et al* 2013, Sharma *et al* 2009).

3. GRAPHENE

Graphene the newly isolated allotrope of carbon, is a single, tightly packed pure layer of carbon atoms collectively bounded in a hexagonal honeycomb lattice that provides rich lode of novel, fundamental and practical applications (Geim *et al* 2008, Novoselov *et al* 2004). Graphite and graphene share the exactly similar basic structural array of their constituent carbon atoms. Each structure begins with six atoms of carbon that are tightly bound chemically together to form a regular hexagon- like benzene ring(Gollavelli *et al* 2013). In otherwords, graphene is an allotrope of carbon in the structure of plane of sp^2 bonded atoms with molecule bond length of 0.142nm. Layers of graphene stacked on top of each other form graphite, with an interplanar spacing of 0.335nm (Huang *et al* 2012, Novoselov *et al* 2012).

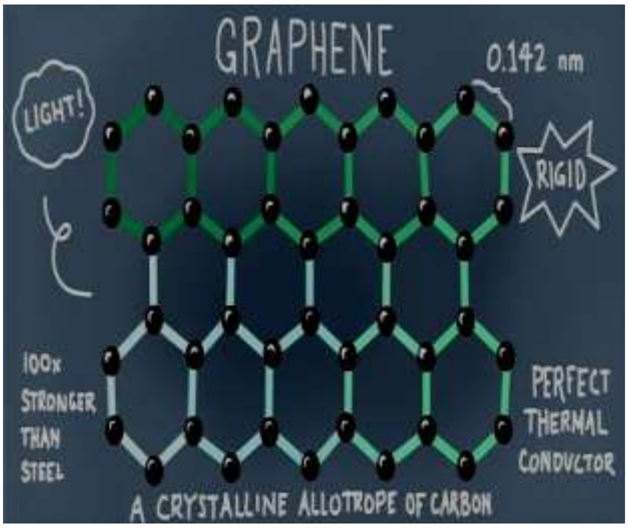

Fig 1: Structure of graphene (aerographene.com)

4. EXCEPTIONAL FEATURES OF GRAPHENE

Graphene, the thinnest material discovered (1 million times thinner than human hair possible on earth), lightest material known (1 square meter: 0.77mg), transparent (200 times stronger than steel), incredibly flexible, best conductor of heat and electricity, all due to the combination of purity and orderliness of the arranged carbon atoms (Geim *et al* 2008, Novoselov *et al* 2004). Perfect crystalline order arises from the strong and extremely flexible interatomic bonds. This creates a substance harder than diamond yet allows the planes to bend whenever mechanical forces are applied. The quality of crystal lattice is also responsible for graphene's remarkable high electrical conductivity (Geim *et al* 2008, Novoselov *et al* 2012).

Graphene has an ultra-large specific-surface area of 2630 m^2/g^{-1} which is an unique feature when compared to other allotropes of carbon (Krantzber *et al* 2012). The exceptional conduction of electrons, moving unimpeded through the lattice at a faster rate attributes the properties of graphene (Geim *et al* 2008, Novoselov *et al* 2004) such as high electron mobility, high opacity due to an one-atom thick fabric of carbon, mechanical strength, exceptionally high electronic and thermal conductivity, impermeability to gases and other supreme properties, all of which is making it a next-generation nano-materials tht can be applied as nanocomposites, nanoelectronics, , nanosensors and nanodevices (Huang *et al* 2011, Novoselov *et al* 2012, Young *et al* 2012).

Carbon, the second most abundant mass within the human body and fourth in the order of most abundant element by mass, followed by hydrogen, helium and oxygen (Geim *et al* 2008) is the chemical basis for all known life forms on universe, and hence graphene could be a sustainable, ecologically friendly solution to an infinite number of applications (Young *et al* 2012). Graphene, since founded, has been applied in various scientific disciplines, with enormous gains being made particularly in chemical, biotechnology and electronics.

5. GRAPHENE OXIDE- AN OXIDIZED PRODUCT OF GRAPHITE

Graphene oxide is functionalized grapheme containing oxygen and chemical groups. It has attracted research interests in recent years due to its superior properties such as surface area, mechanical stability, optical and electrical properties (Dreyer *et al*. 2009). The surface functional groups of hydroxyl, carboxyl and epoxy make graphene oxide an excellent material when combined with other materials and molecules (Liu *et al*. 2012).

Functional groups of graphene oxide exhibit strong acidity, high adsorptivity for basic compounds and cations. Graphene provides hydrophobic surface, superior mechanical properties that exhibit high adsorption due to strong π- π interaction. Graphene possesses superior mechanical properties than graphene oxide, but they both provide equal levels of stiffness and strength (Young *et al* 2012). These new carbonaceous materials, effectively adsorb diverse gaseous and aqueous pollutants (Wang *et al* 2013)providing a promising arena that promotes nitrate removal from water (Motamedi *et al* 2014).

Table 1: Maximum adsorption capacity of various absorbents of nitrate

Adsorbent	Amount of Nitrate Absorbed (mg/g)	Specific Area (m^2/g)	Reference
Magnesium Oxide –Biochar	94		Zhang *et al* 2012
Acid Treated Sepiolite	38	515	Ozturk *et al* 2004
HCl Treated Red Mud	363	20.7	Cengeloglu *et al* 2006
Activated Carbon Cloth (H_2SO_4)	126	2500	Afkhami *et al* 2007
Protonated Cross-linked Chitosan	104	-	Chatterjee *et al* 2009
$ZnCl_2$ Treated Coconut Coir Pith	10.3	910	Namasivayam 2005, 2008
$ZnCl_2$ Treated Activated Carbon	27.6	1826	Demiral *et al* 2010
Zirconium Oxychloride-Sugar Beet Pulp	63	-	Hassan *et al* 2010

6. REMOVAL OF NITRATE USING GRAPHENE NANOCOMPOSITES

In recent past, graphene, graphene oxide and their altered forms can be applied as good materials for nitrate removal.

Catalyst such as palladium-copper held by graphene with Fe^0 reductants showed 82% of nitrate removal and 66% of N2 selectvity (Yun *et al* 2016).

Magnetic graphene nanoparticles (G-Fe3O4 MNPs) using Taguchi experimental design and parameters were optimized batch reactor by Minitab software. The results revealed that in optimized condition (pH-3, contact time-60min, initial concentration-50mg/L, ,temperature-50°C, adsorbent dosage-2g/L) 86.4% of nitrate removal was achieved. G-Fe3O4 Magnetic nanoparticles is an effective sorbent for removal of nitrate from water because of its easy, rapid and high nitrate removal efficiency (Ghanizadeh *et al* 2015).

Nanocomposites material nano-scale zero valent iron, activated carbon can remove nitrate up to 94.3%. Nanocomposites material showed high efficiency in removal of nitrate compared to nanoscale zero valent iron (Liu *et al* 2016).

Nitrate removal from water can be achieved by coating nickel and cobalt nanoparticles with graphene oxide. Iron, nickel and cobalt with novel and unique properties of graphene based nanocomposites which showed outstanding performance in nitrate removal from water (Motamedi *et al* 2014).

7. CONCLUSION

Graphene is one of the highly potential materials which have led to a cascade of diverse international research and infinite technologies especially in water purification technology.

Practicability of using graphene, graphene oxide and nanocomposites is enormous in denitrification of groundwater due to exceptional properties including and also ultra large specific-surface area which contributes largely in enhancing the adsorption capacity in removal of nitrate from groundwater.

ACKNOWLEDGEMENT

We wish to acknowledge Department of Chemical Engineering, M S Ramaiah Institute of Technlogy, Bengaluru for all the support extended.

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