DENITRIFICATION OF GROUNDWATER USING GRAPHENE, GRAPHENE OXIDE AND NANOCOMPOSITES

Bhagyeshwari D Chalageri\(^1\), Archna\(^2\), Rajeswari M Kulkarni\(^3\)

\(^1\)Department of Chemical Engineering, M S Ramaiah Institute Of Technology, Bengaluru-560054 Karnataka, India
\(^2\)Department of Chemical Engineering, M S Ramaiah Institute Of Technology, Bengaluru-560054 Karnataka, India
\(^3\)Department of Chemical Engineering, M S Ramaiah Institute Of Technology, Bengaluru-560054 Karnataka, India.

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

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 volatilization 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 al 2014, Loganathan et al 2012, Shrimali et al 2001).

Prominent levels of nitrate in potable water can cause many health problems like stomach cancer, methemoglobinemia (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 sp² 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).

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 m²/g 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 that 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 graphene 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>
<thead>
<tr>
<th>Adsorbent</th>
<th>Amount of Nitrate Absorbed (mg/g)</th>
<th>Specific Area (m²/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium Oxide –Biochar</td>
<td>94</td>
<td>-</td>
<td>Zhang et al 2012</td>
</tr>
<tr>
<td>Acid Treated Sepiolite</td>
<td>38</td>
<td>515</td>
<td>Ozturk et al 2004</td>
</tr>
<tr>
<td>HCl Treated Red Mud</td>
<td>363</td>
<td>20.7</td>
<td>Cengeloglu et al 2006</td>
</tr>
<tr>
<td>Activated Carbon Cloth (H₂SO₄)</td>
<td>126</td>
<td>2500</td>
<td>Afkhami et al 2007</td>
</tr>
<tr>
<td>Protonated Cross-linked Chitosan</td>
<td>104</td>
<td>-</td>
<td>Chatterjee et al 2009</td>
</tr>
<tr>
<td>ZnCl₂ Treated Activated Carbon</td>
<td>27.6</td>
<td>1826</td>
<td>Demiral et al 2010</td>
</tr>
<tr>
<td>Zirconium Oxichloride-Sugar Beet Pulp</td>
<td>63</td>
<td>-</td>
<td>Hassan et al 2010</td>
</tr>
</tbody>
</table>

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 Fe²⁺ reductants showed 82% of nitrate removal and 66% of N2 selectivity (Yun et al 2016).

Magnetic graphene nanoparticles (G-Fe3O4 MNPs) using Taguchi experimental design and parameters were optimized batch reactor by Mininab 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 Technology, Bengaluru for all the support extended.

REFERENCES

[6] xxZa


