Superiority of Graphene over Activated Carbon in terms of Adsorption Capacity, Proposed Mechanism and Interaction with Metal Ions and Biological Particulates

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Abstract: *To tackle the on-going pollution and various contaminants in the ecosystem and to ensure availability of ambient conditions of natural resources like air and water, there is an alarming demand globally for developments in high performance purification materials/ devices. This paper is a review of performance of two of the most widely discussed carbonaceous materials often spoken about in the context of filtration and contamination - the conventional Activated Carbon (AC) along with its modified forms and the relatively new 2D counterpart Graphene. Our study describes how the 2D Graphene and its composite structures possess considerable superiority over AC in terms of adsorption capacity and efficiency in interacting with ions and pathogens like viruses and bacteria. The superiority in properties can be attributed to high surface area per unit mass, distribution of surface functionality, pH tolerance and higher multisite adsorption due to large number of surface functional groups. The review has a vital role in predicting possible areas of applications where Graphene has potential to replace AC.*

Keywords: Graphene, activated carbon, oxide of graphene,

1. Introduction

The extend of industrialization and environmental pollution continue to increase at an unprecedented rapid pace. We also face a constant threat of being infected by pathogens which may sometimes even challenge our existence in this planet. Industrial discharges and fumes containing high concentration of toxins like pharmaceuticals, pesticides, dyes containing heavy metal ions like Pb, Cr, Cd, and Cu; when released into the environment are highly toxic and can bio-accumulate in human body, aquatic life, atmosphere and in soil [1]. In fact, metal contamination is found to be a major problem in disposing industrial and municipal wastewater [2]. These contaminants when present in atmosphere can cause great degree of health hazards, especially to the more vulnerable ones like children, pregnant women, elderly people and allergic people.

Pathogens like bacteria and viruses can also have significant health implications in humans as well as animals [3]. To tackle the situation, various chemistry based efforts have been devoted to feasibly control the impact on human health and environment, also to filter out these contaminants from the environment. Among various methods of treating the industrial effluents like electrochemical treatment, reverse osmosis filtration, evaporation recovery and electrocoagulation [4-6]. Among these all technologies, adsorption is relatively new and is found to be comparatively superior in terms of efficiency, rapidness, cost effectiveness and environment friendly method. Many papers have been published in the past few decades, confirming the carbonaceous materials are effective adsorbents for decontamination of metal ions and their complexes [7]. Activated carbon (AC) being one of the first material applied as adsorbent, has been utilized in numerous applications due to its excellent adsorption capabilities, attributing to its large specific surface area and highly porous internal structure.

Studies show successful role of AC in the adsorption of heavy metal ions [8]. Another research shows successful adsorption of polio virus and infectious hepatitis virus on AC [9]. Through introduction of different acidic/oxidative or basic surface functionality, AC can be modified to increase selectivity of certain species. However, this limits the adsorption of other contaminants, making AC more selective to specific species only.

This turns to be a major disadvantage in an environment where numerous species co-exist, as in water bodies and atmospheric air. Relatively low evidences of work have been found to prove an appropriate balance of selectivity on AC or to show the effect of competitive adsorption and any positive or negative effects that can arise from complex mixtures [10].

Talking of the newly developed counterpart Graphene, a fascinating new member of the carbon family, this hypothetical one-atom thick sheet has sp_2 hybridized carbon bonded to each other; forming a honeycomb 2D lattice. Graphene is one of the most fascinating nanostructure with unique physical, chemical, electrical and mechanical properties [14] which qualifies it as a promising nanomaterial in material science [11,12] and a wide range of technological applications like bioelectronics and bio sensing [13]. The oxide of Graphene, generally prepared by Hummer's method or modified Hummer's method [18] from Graphene, which is basically an acid treatment process, GO's specific surface area indicates it can be used as an efficient adsorbent. The topological variation can result in different interactions between the carbon substrate and a guest molecule and consequently, variation in adsorption behaviour [15]. Studies show that GO is more efficient than AC in adsorption of metal ions [15]. Destruction of peptidoglycan in bacteria(cytotoxicity)[16], inactivation of virus by destruction of capsid structure as well as lipid envelop[17], can be attributed to physicochemical interactions(like mechanical strength, magnetism, hydrophobicity etc) which could primarily ascribe hydrogen binding, electrostatic interaction and redox reaction.

Herein, we discussed the adsorption behaviour of AC and Graphene (oxides) for metal ions and pathogens like Bacteria and viruses based on the characterization of these two carbonaceous materials, analysis of adsorption isotherms, Buffer capacity (i.e. pH effect on adsorption) and effect of adsorption due to surface functionalities. We further extend our discussion to some of the crucial findings that highlight the fact that Graphene exhibit a clear superiority over AC, which can possibly open door for further studies to develop the next generation regenerative filtration and purification devices/mechanisms with enhanced functionality and stability.

2. Analysis and Discussion:

Adsorption being a surface phenomenon, higher specific surface area plays the most important role in determining the adsorption capacity of a material (table 1). 2D materials like Graphene possess high aspect ratio as compared to the 3D structure. Further, the presence of internal atoms in the lattice limits the adsorption capacity. The promising aspects of 2D nanostructures like Graphene and CNTs to be used in adsorption process is that they give higher adsorption for relatively low quantity of material.

Table 1: Physical properties of GO and AC [15]

	Specific surface Area(m_2/g)	Pore Volume(cm_3/g)
GO	148.34	0.091
AC	28.64	0.038

A detailed discussion of the interaction of these two carbonaceous materials with various contaminants mentioned earlier have been analysed in the following sections.

2.1 Adsorption analysis of metal ions on AC and GO:

Adsorption of methylene blue dye on GO was attributed to π-π electron donor acceptor interactions and electrostatic interactions, however while that on AC was due to large surface area [19]. Another study on the suggests that AC materials have the capacity to form cation/ anion-π interaction with metal species, but this process is generally extremely poor, hence not considered.

A study on the adsorption of Cu ions suggest that AC has lower adsorption efficiency than GO under acidic condition [15]. The maximum adsorption capacity for GO was found to be 1.18 X 10-3 mol g-1 and that for AC was much low, at around 2.31 X 10-4 mol g-1; as found from the Langmuir's adsorption isotherm. The study also suggested Langmuir model to be more accurate for metal ions like Cu(II) as compared to the Freundlich model. Further, potentiometric acid-base titration experiment on these carbonaceous materials reveal that the buffer capacity of GO>AC. The buffer capacity can be assigned to the concentration of surface functional groups, that was found to be 6 times higher in GO than on AC. The affinity of Cu(II) ions towards GO and AC .

GO>AC. This can be correlated with the pH_{pzc}(GO)< pH_{pzc}(AC). pH_{pzc} controls the Coulombic interactions between carbonaceous surface and the aqueous metal ions and hence the metal ion uptake [20]. PHpzc value depends upon the surface acidic functional groups[21] . The higher the concentration of surface acidic functional groups, lower the value of pH_{pzc}, suggesting the reason for higher efficiency of Cu(II) ions decontamination using GO. Another remarkable conclusion that can be drawn out from the pH_{pzc} discussion is the higher concentration of the surface acidic or oxidative functional groups in GO.

Other major heavy metal ion contaminants that are found to be highly toxic apart from Cu(II) are Pb(II), Cd(II),Cr(VI) [22] is also found to have a similar trend in adsorption as that of Cu(II) ion. The adsorption capacity of GO and AC for Pb(II) and Cd(II) metal ions is shown in Table 2.

Table 2: Adsorption of Pb and Cd ions on AC and GO [2]

	Adsorption capacity (mg/g)		
	AC		GO
	Native	Modified	
Pb(II)	66.23	95.24	447
Cd(II)	N/A	1.98	177

It is evident from this table that GO-composites possess tremendously high adsorption capacity for these ions as compared to even the modified acidic - functionalized AC.

2.2 Adsorption analysis of bacteria on AC and Graphene:

Using native AC in the application where bactericidal properties are needed is found to be a problem. Studies show that AC may adversely affect by favouring environment for the growth of microorganisms. Hence, an alternative that is being employed to produce AC with antimicrobial properties is its modification with silver nanoparticles (AgNPs) that are commonly used as microbial agents [28].

A study shows that some unique properties of graphene nano sheets are similar to the properties of CNTs. This is a vital implication of potential of graphene to be used in this field.

Earlier studies suggest, single wall CNTs present noticeable cytotoxicity to human and animal cells[32,33]. Also, toxicity of SWCNTs is greater than MWCNTs; which can be associated to oxidative stress[32,34] cutting off the intercellular metabolic routes [34] and rupture of cell membrane [35]. However, oxidative stress is rega Experiments performed to check interaction of gram (+) and gram (-) with metal impregnated AC [25, 26] especially AgNPs, CuNPs, ZnNPs and PbNPs had shown successful results in adsorption data when analysed by UV-Vis Spectroscopy and FT-IR Spectroscopy. Although these in-vitro results are limited by the high cost of manufacturing metallic nanoparticles and problems of aggregation of metal ions in the dispersion due to interparticle surface attraction and release of metal ions from metallic nanoparticles which is attributed to the oxidation process[27].

Bacterial toxicity of the graphene nanosheets in the form of graphene nanowalls [16]; capture of bacterial species and particulates which cause severe nosocomial infection in patients and health care workers by a porous conductive graphene material called Laser Induced Graphene(LIG) obtained from CO2 laser cutting of simple polyamide film[29] which employs periodic Joule heating (>300°C) that only destroys bacteria but any other microorganisms that possess potential to cause adverse biological reactions and diseases (like pyrogens, allergens, exotoxins, endotoxins, mycotoxins, nucleic acid and prions); studies made on the graphene materials and composite for neutralizing microorganisms function through different mechanism including penetration and compromisation of the bacteria membrane, generation of reactive oxygen species(ROS) and envelopment of microbes[30,31] are few critical studies mentioned among the large number of other successful studies implying the use of graphene and it's composites for antibacterial action.

Hence, we postulate that Graphene is far superior to AC and it's modified forms in terms of effectiveness of bacteriocidal effect and in general, cytotoxicity considered as the most acceptable mechanism. Extending this subject to graphene nanosheets with extreme high aspect ratio can be proposed as one of the excellent and ideal nanostructure for the application. Further, a study shows that the graphene oxide nanowalls(GONWs) obtained by Electrophoretic deposition (EPD) process good cytotoxicity to bacterial cell [16].

However, on reducing GONWs with Hydrazine as reducing agent in the suspension, reduced graphene nanowalled structure (RGNWs) were produced. RGNWs possess higher toxicity than GONWs. To determine the bacterial toxicity of both GONWs and RGNWs their effect on a gram (-)ve bacteria (E.coli) and a gram (+)ve bacteria (S.Aureus) was analysed. The result of the experiment after 1 hour is tabulated below[Table 3].

Table 3: Antibacterial activity of GONWs and RGNWs [16]

Sample	Antibacterial Activity (in 1 hour)	
	{Survival Bacteria (%)}	
	E.coli	S.aureus
GONWs	41(±8)	26(±5)
RGNWs	16(± 3)	5(± 1)

These result shows that RGNWs works better for antibacterial applications.Further extension in the time of experiment to upto 2 days showed 100% antibacterial activity, proving RGNW to be one of the most efficient nanostructure for the application. This can be attributed to stronger interaction between more sharpened edges of reduced nanowalls with the cell membrane and/or better charge transfer between the bacteria and edges of RGNWs.

Further, the reason for the relatively low inactivity of gram (-ve) bacteria E.Coli as compared to the gram(+)ve S.Aureus may be attributed to the pressure of thin peptidoglycan layer in E.Coli, this inhibiting the interaction of bacteria to the lateral plane of RGNWs. Reverse is the case for gram (+)ve S.Aureus which possesses a much thicker peptydoglycan layer resulting in higher affinity to graphene nanowalled structures.

2.3 Adsorption analysis of viruses on AC and Graphene:

Considered to be the mo.st mischievous pathogen to humans, animals as well as plants; wide range of viruses have infected the human race in various ways time-to-time and continue to do so. A study by John T. Cookson Jr.[36] describes in his study, how the virus can be adsorbed by Activated Carbon and possible mechanism behind it. It is worth mentioning here, that even earlier, activated carbon has successfully adsorbed Polio virus and infectious Hepatitis virus [9].

In this study[36], Coliform bacteriophage was used; as the knowledge of phage properties are advanced for bacterial cell (E. coli B cells were used in this study). Inspite of using a bacteriophage, adsorption characteristics of human-infecting viruses can be concluded from the study, as bacterial virus exhibit similar adsorption characteristics. Adsorption of virus on AC is greatly dependent on the pH of the solution or atmosphere, in which adsorption takes place. A decrease in pH from the optimum of 7 is found to decrease in pH the rate of adsorption, probably due to inability of carboxyl group surface functionality of AC to get ionized at low pH. However, at higher pH, positively charged amino acid groups of viruses protein shell interact with the negatively charged carboxyl groups of carbon. Such high dependency of virus and AC on the surrounding pH is a limitation for its application, which can which can also be attributed to the low Buffer capacity of of the AC[15]. Moreover, esterifying of carboxyl groups may lead to blockage of adsorption sites[36] resulting in drastic decrease in the adsorption capacity. However, there is no evidence of lipid enveloped viruses being adsorbed on AC.

Graphene's capability to interact efficiently with bacterial membranes by direct inorganicbiomolecule interaction have been discussed earlier in this paper. The interplay between GO and microbes have been demonstrated, attributing to the bioreduction of oxygen containing functionalities via bacterial respiration. Considering the versatile GO biomolecule interactions, we can reach to a conclusion that GO materials could potentially serve as a novel nanostructure for virus prevention.

This can be associated to the multiplex biological interaction between GO nanosheets and viruses. To get an insight of the answer to the question of why Graphene can act superior to AC in virus capture; we discuss the results of a study conducted on two enteric viruses, namely EV71 and H9N2[17].

In this study, the viruses were exposed directly to GO suspension (50µm/ml) at different temperatures for about 30 mins. . The disinfectant effect of GO was found to be weak at room temperature (25^{o}C). However, increase in the temperature marked as adsorption enhancement. This dependency of adsorption to elevated temperature and prolonged exposure time is being explained by another study[38]. The analysis of GO-Virus interaction can be studied from the results of UV-Vis spectroscopy. It shows strong protein adsorption capacity of GO. This unique physicochemical interactions can be attributed to Hydrogen binding, electrostatic interactions and redox reaction.

The FT-IR spectroscopy analysis of the interaction suggests some major deductions, which is extremely useful for reasoning of GO to be highly effective nanostructure over virus adsorption. The results suggest that GO relatively bioreduced in the presence of these viruses (i.e. EV71 and H9N2) to reduced GO(rGO) . The viruses were found to thermally reduce GO[39].

Hence, the capture of virus Particles may be explained as the physicochemical interaction between various oxygenated group on the GO surface and the viruses. Further, evidences of general disruption effect of GO have been observed successfully in various studies, siting disrupted virus particles both on the edge as well as the basal plane, implying effective destruction of both capsid(protein) coated viruses and lipid coated (enveloped) viruses.

3. Conclusion and Future Perspectives

The discussions made in this review points towards a quite clear picture of why the title of this paper is "Superiority of Graphene over AC". Be it in terms of larger specific surface area or multiplex trapping of the pathogens. One of the promising aspects of Graphene-based material over AC is its capability to regenerate its surface function groups, which is likely to be of use in next generation purification devices. The size-exclusion properties of graphene Nano mesh and tuneable size of Nano pores are the contributions which would help in achieving ultrafiltration and water desalination in the next few decades.

Activated carbon , due to its current cost of manufacture, remains the most prominent carbon – based adsorbent, and used in a wide spectrum of applications. However, the potentials of Graphene realized by researchers and nano- scientists cannot be neglected.

Though technical problems exist in taking out the laboratory finding on Graphene to an actually usable scale; the developments in the high precision Nanoprocessing promises that Graphene would soon take over, marking as the start of a new era in material science, probably calling it Graphene Era!

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