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Synthesis and Analysis of Graphene Nano Composite

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Abstract: Graphene based composites have various applications in the modern world. In which synthesis of effective composite suitable for applications is a challenging task. One among the application area of graphene composite is in wastewater treatment. Water pollution is now a days consider to be a major global health and environmental issue affecting all ecosystems as well as life forms. While considering pollution the most dominant in creating pollution is found to be the industries and factories. Saying about the industries the available facilities in the water treatment is found to be the major challenges in treating of polluted water caused by heavy metals and dyes. In factories, only lower stage of wastewater treatment is alone found to be available. Some of the industries they are installing economical based treatment plant to manage the government policies and not following the pollutant removal completely. In such case, lower level pollutants alone found to be removed and higher-level hazardous metals and dyes are found to be not removed generally. To overcome such situation and support industries as well as factories introduction of economical adsorbent to remove the waste is the major proposal. This paper discusses various graphene-based adsorbents persisting in the removal of dye and heavy metals as well as synthesis of efficient Composite.

Keywords: Graphene, Adsorbents, Dye, Heavy Metal Ions, Water Bodies, Pollutant Removal

1. Introduction

In several decades, the environment gets polluted and became high level of contamination with chemical hazards namely heavy metals and synthetic dyes due to proportional increase of domestic and industrial activities in parallel with human population growth. These pollutants have described about cause of accumulated toxicities and the effects of carcinogenic on the living organisms and human bodies [1-3].

A wide range of wastewater treating method namely membrane filtration, ion exchange solvent extraction, flocculation, cementation, electro-coagulation and adsorption which is used for removing waste water, municipal and potable are shown in Figure-1.

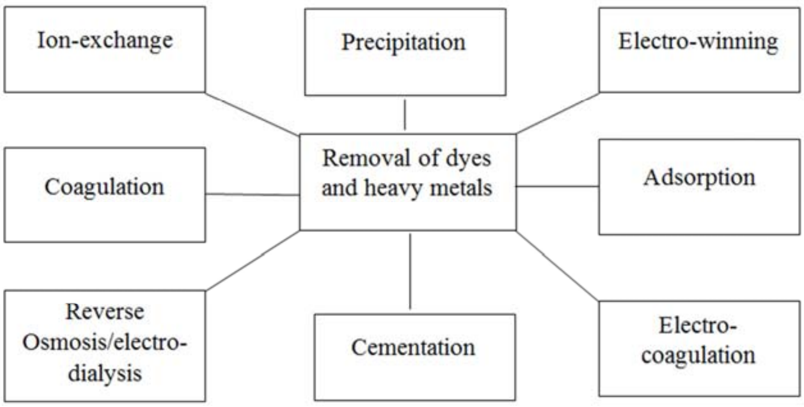


Figure 1. *Removal of heavy ions and dyes using conventional methods.*

There are several water purification methods have been developed in order to reduce the water pollution effects whereas adsorption is the most effective method due to its ease in operation with less cost. The adsorbents have large range that are used for removing those pollutants but the efficiency of absorbents get varies with type which is described in Table-1 on the basis of the respective adsorption capacity.

Table 1. *Adsorbents used for the removal of different dyes and heavy metals.*

Adsorbent	Pollutants	q_m(maximum adsorption capacity)(mg/g)
Biomass		
Coffee Residue	Cu^{2+}	70.0
Luffa Acutangula Peel	Malachite green	69.64
Litchi Peel Waste	Cr^{6+}	101.1
Cortaderia selloana Flower Spikes	Methylene blue	114.3
Fish Scales Waste	Acid Blue 113	145.3
Clays		
Aluminium Pillared Clay	Hg^{2+}	49.75
Bentonite	Phenol	66.67
Safi decanted Clays	Malachite green	88.70
Polymer matrix		
Alginate Beads	U^{6+}	237.15
Activated Carbon	Cu^{2+}	43.47
Biochar	Pb^{2+}	20.87

Recent research have demonstrated the potential application of low dimensional carbon nanomaterials such as graphene (Zhu 2017), Carbon Nanotube (CNT) [5] and fullerene [6] have high adsorbent efficiency in capturing enormous water pollutants. In particular, graphene is fascinated with essential research interest for the possible uses in several fields namely medical, electronics, material science and environment [7]. In general, graphene features get empowered its distinct application namely Adsorption, Energy Storage, Electronic Devices, bio-sensing and reinforcement of composite material [9-16].

1.1. Pollutant of Heavy Metal

In general, heavy metals are specified as metalloid or dense metals based on atomic weight ranges from 63.5 to 200.6 Dalton and with specific gravity>5 g/mL[17-18]. Get classified into three categories such as radionuclide, toxic metals and precious metals. The activities of intensive industrial are fertilizer manufacture, painting, electro plating, Cd-Ni battery manufacture, mining and smelting have cause serious pollutant of heavy metal in the environment of aquatic [19]. The heavy metals formation have created fatal damages for the human bodies and to aquatic environment whereas they are high toxic and non-ecological [20-21]. The health hazard caused due to heavy metals were detailed and are shown in Table-2 [22-23]. Precious metals such as palladium (Pd), platinum (Pt), silver (Ag), gold (Au) and ruthenium (Ru) have high commercial value, as they are rare in nature [24]. Thus, the discharge of wastewater containing heavy metals needs to be regulated to safeguard the environment and human health. To regulate emissions to the environment, many countries have imposed specific discharge limits for the heavy metals such as the Malaysia effluent discharge standards, United States Environmental Protection Agency (USEPA) maximum contaminant level, World Health Organization (WHO) guideline standard and China integrated wastewater discharge standards, as shown in Table 2.

Table 2. *Health hazards and discharge limits of heavy metals.*

Heavy metal	Discharge limits Standard	WHO Guideline Standard
Cd	0.010	0.003
Pb	0.100	$0.010^{(p)}$
As	0.050	$0.010^{(p)}$
Ni	0.200	0.070
Mn	0.200	$0.400^{(H)}$
Sn	0.200	-
Hg	0.005	0.006
Cu	0.200	2.000
Fe	1.000	$0.300^{(N)}$
Ag	-	-
U	-	$0.030^{(p)}$

1.2. Dye Pollutants

In several industries namely paint; cosmetic, pigment manufacturing and paint sectors have widely used synthetic dye as a coloring agent [25]. Moreover, 7 million tons of dye have produced per year as worldwide [26-28]. The frequent acceptance of its application or ionic charges is done due to chemical structure complexity. The described classification has been shown in Table-3. It has segregated synthetic dye into cationic, nonionic and anionic dyes. In general, non-ionic dyes namely disperse and vat dyes are easily insoluble in water but can be soluble in organic solvents. Similarly, ionic dye can easily soluble in water that is further more classified as cationic and anionic dyes. All basic dyes are known as cationic dyes, while anionic dyes are made up of three categories, which are acid, direct and reactive dyes. Nearly 10-15% of the substance is released with contaminated water from the dye manufacturing [29] whereas treatment facility of wastewater with inability has created dye for entering into environment. When the dye concentration is less or equal to 1 mg/L can easily able to detect the water contamination based on coloration of the water bodies received [28]. These dye molecules have observed and diverted the entering of sunlight in the water bodies which hinder the rate of photosynthesis in aquatic plants. The synthetic dye with exposure of protracted have a result namely respiration problem, skin irritation and even cause cancer [30]. Synthetic dye molecules are designed and made to be resistant against washing water, chemicals, heat and ultraviolet light, making them very difficult to be treated by standard wastewater treatment facilities.

Table 3. *Dye example based on properties and classification.*

Dye Type	Substrate	Chemical groups	Example
Acid	Inks, paper and leather	Triphenylmethane, Azo, xanthenes, anthraquinone and nitro	acid fuschin, indigo carmine, , acid black 2 and acid yellow 17
Reactive	Silk, wool, textile and cotton	Formazan, Azo, oxazine, phthalocyanineand anthraquinone	Reactive red 120 and reactive blue 4 and
Basic	Antiseptics medicine and treated nylon	Oxazine, acridine, xanthene and azinediphenylmethane	Orange 2, malachite green, basic fustian and rhodamine 6G
Vat	Indigoids and anthraquinone.	Cotton, wool and cellulose fiber	vat yellow 20,vat green 9 and vat blue 4 and

2. Synthesis of Graphene Adsorbent

Considering various adsorbents graphene based are seems to be very effective. From the chronicle survey of graphene adsorbents, they are familiar due to their efficient characteristics. As a preparation of efficient graphene adsorbent synthesis of reduced graphene oxide aerogel, which is used as best option in wastewater treatment. The pristine graphite has invoked the GO preparation are included as general exfoliation and oxidation which is protracted in producing rGO through the process of reduction is shown in Figure-2. There are various GO synthesis routes have advanced among the past decade namely brodie method [31], Stauden maier technique, Hoffmann technique [32] and Hummers technique [33] along with its altered and enhanced version is shown in Figure-2.

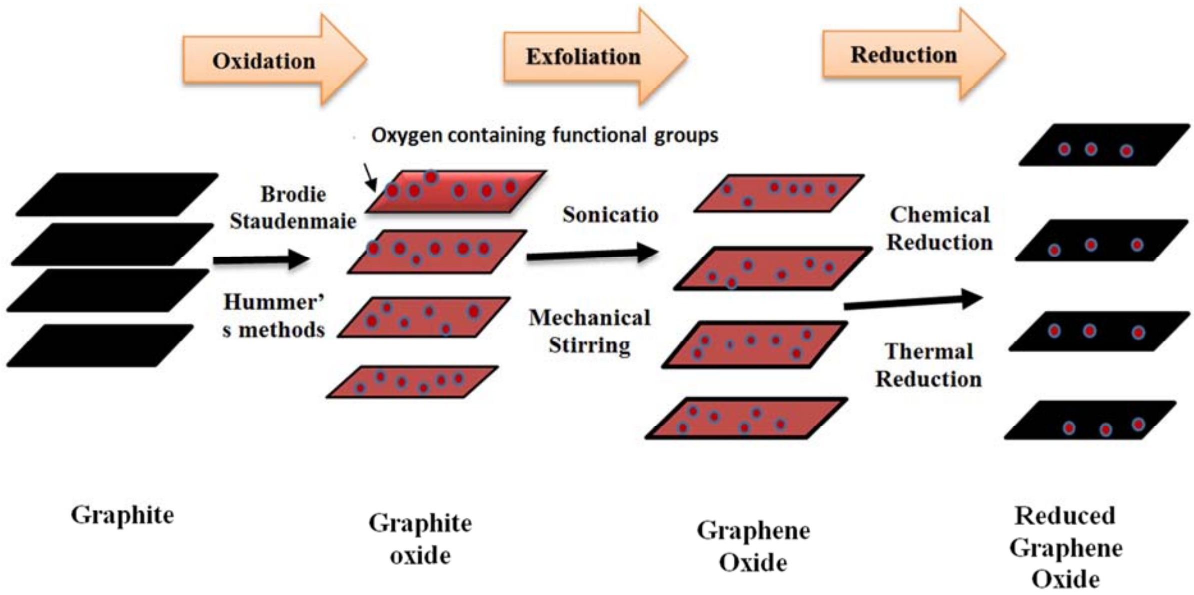


Figure 2. *Conventional processes in the GO synthesis and rGO using pristine graphite.*

The long reaction time that ranges from 72 to 96 hours is one of the major problems in brodie technique and toxic gaseous releases along with its by-products. The method of Stauden maier is the enhancement of Brodie method that has increased the reaction level of acidity by introducing conc. Sulphuric acid (H_2SO_4) that resulted with the single reaction of vessel system. However, this method has consumed less time and produce chlorine dioxide which is an explosive. After some year passed, Hoffmann has deduced the synthesis risk level using non-fuming of nitric acid (HNO_3).

Freeze drying

This process is generally accomplished for removing the water molecules that is fascinated within the rGO hydrogel structure to create a methodical configured aerogel [38-40].

The rGO aerogel prepared from sheet of GO has considered in three major steps is shown in figure-8. The reduction process is used in general for transferring the GO sheets into rGO hydrogel whereas hydrogel made freeze is the next step for crystallizing the water molecules. This water crystal performs to be a forming agent. Therefore, purification of solidified water molecules is done through vacuum condition in order to produce an rGO aerogel in 3D porous.

This 3D graphene based aerogel with porous microstructure is extremely reliant on hydrogel nature, temperature gradient and condition of freezing. The high conductive nature of graphene-based aerogel along with stability in mechanical are created. It has explored two purification system types involved that are super critical CO2 and freeze drying [41]. It states that graphene aerogel produced using super-critical CO2 drying has exhibit the significant mechanical properties which have endure 14,000 times of its self-weight than that prepared by freeze drying (3300 times its own weight). The aerogel prepared by super-critical CO2 showed a BET surface of 512 m^2/g, which was higher than that of aerogel prepared by freeze drying (11.8 m^2/g). It has explored the reduction agent significant namely ammonia, ethanediamine (EDA) and vitamin C on the pattern of graphene aerogel using the technique of hydrothermal whereas the graphene aerogels surface area have reduced using vitamin C, ammonia and EDA is noticed as 661, 1089 and 440 m^2/g, correspondingly [42].

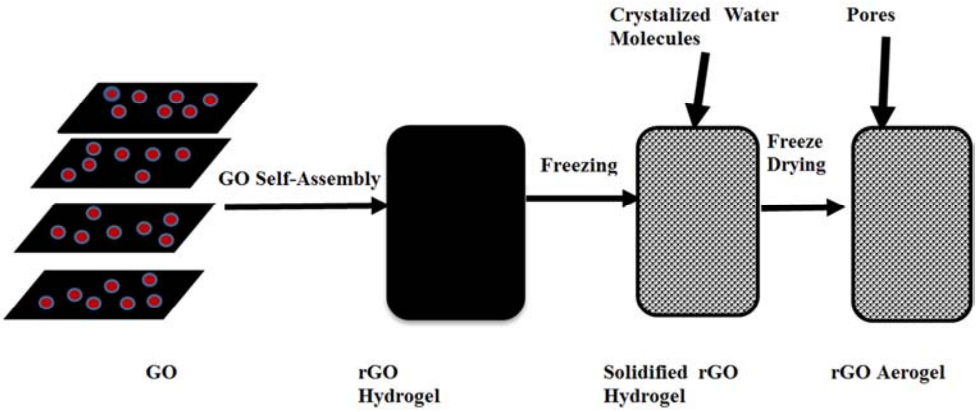


Figure 3. *RGO aerogel synthesis by freeze-drying.*

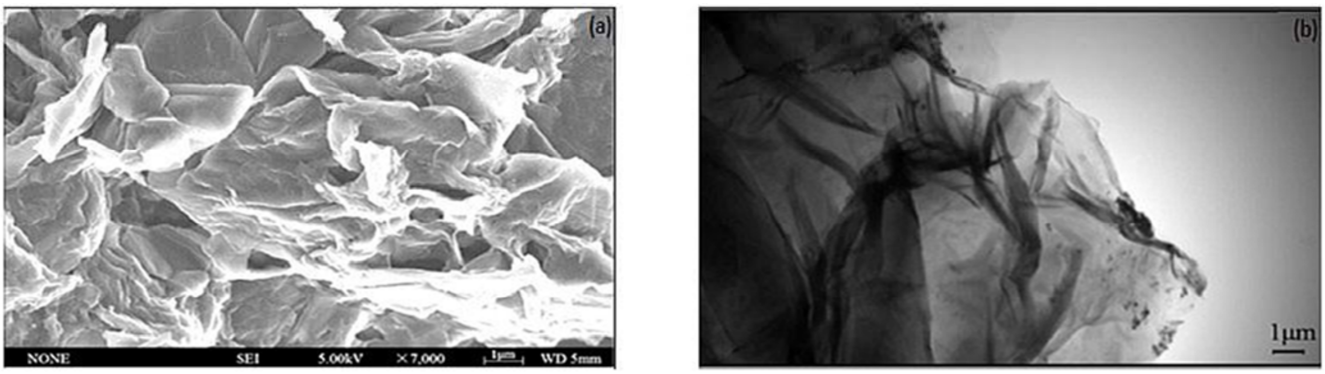
However, the highest mechanical strength was demonstrated by the VC-reduced graphene aerogel. The researchers further reported that the surface roughness could be governed by the pH values that were determined by the functional groups of reducing agents. This study deals with PH value for mixture solution EDA-GO, ammonia-GO and vitamin C-GO in prior to hydrothermal reductions are 3.4, 10.4 and 11 correspondingly.

During the process of reduction, graphene sheet agglomeration and fragmentation based on acidic condition has been promoted. Hence, the fundamental condition has selected the larger production graphene sheet using thin morphology [42-44].

Chemical structure and properties of graphene-based materials are given in Table 4.

Table 4. *Chemical structure and properties of graphene-based materials.*

Material	Graphene	GO	rGO
C:O ratio	No oxygen	2 - 4	8 – 246
Young's modulus (GPa)	1000	200	250
Electron mobility (cm^2/V s)	10000 – 50000	Insulator	0.05 – 200
Production cost	High	Low	Low



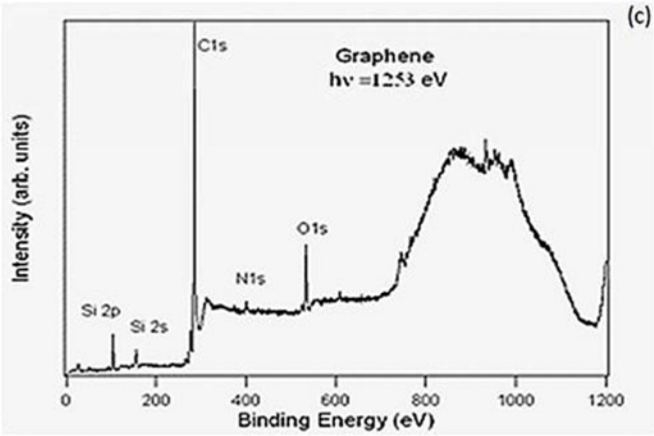


Figure 4. *SEM image (a), TEM image (b), and wide XPS scan of cleaved UITAR (c) of graphene.*

Figure. 4(a) the flocculate in the absence of external forces will remain stable, and it is difficult to separate them from each other. The thickness of graphene was determined accurately by TEM taking large number of images to generate a series of thickness statistic. In Figure. 4 (b), the graphene layer stacking disorder is clearly displayed. It is essential that establishment of hydrocarbon atom in the process of oxidation has led to the sp^2 disturbance in carbon layer and additionally, the thermal stability has assured that graphene with thin layer is provoked their impulsive wrinkled and staking characterization. Stankovich provided the elemental characterization of graphene powder by XPS as shown in Figure. 4 (c).

3. Conclusions

Presence of dye and heavy metals due to contamination in the environmental water bodies is one of the major causes of water pollution. In order to reduce contamination of water bodies the wastewater from various sources needs to be filtered effectively such that water pollution is diminished. To carry out that graphene based adsorbent had been implemented and the process of synthesizing had been elaborated. From the characteristic analysis, the proposed reduced graphene oxide is found to be efficient.

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