Facile Synthesis of Nanostructured ZnO-rGO based graphene and it’s Application in Waste Water Treatment

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Abstract

In the present work graphene oxide GO prepared by chemical exifliaion of graphite using Hummer’s method. A facile and green synthesis of ZnO-rGO nanocomposite was performed via Alovera plant extract. The characterization tools (XRD-FTIR- FESEM-TEM- AFM) proved the formation of single phase of ZnO-rGO nanocomposite. Since the environmental contamination caused by Cd(II) ion is a world issue as it has a harmful effect especially on the human health and environment. Subsequently, our goal in this work is to find an accurate method for detection and adsorption of toxic Cd(II). ZnO and ZnO-rGO nanocomposites are prepared for removing Cd(II) and on behalf of increasing its removal efficiency, GO is added. The results showed a great improvement in removal efficiency reached up to 90% at pH 6 after 90 min. the structure and surface of prepared samples studied through XRD, FTIR, FESEM and AFM.

KeyWords

Graphene Oxide; ZnO-rGO nanocomposite; Waste Water Treatment; Heavy metal removal
1. Introduction

Synthesis, properties and applications of graphene based nanocomposites materials have attracted tremendous attention nowadays [1-10]. Since the insoluble graphene has limited application without functionalization by metal oxides. Among many methods of preparing the soluble graphene oxide and its reduced form, chemical reduction of graphene oxide is the most popular method. Chemical reduction methods generally use toxic and high cost reducing agent e.g hydrazine hydrate [6-8]. To overcome this disadvantageous, some plants extracts is used for reduction of graphene oxide [9-10]. These methods are low cost and echofriendly. In this work Alovera plant extract is used to reduced graphene oxide and preparation of ZnO-rGO nanocomposite for waste water treatment.

Since the pollution of heavy metals in waste water is one of the main challenges faced via environment and human health [11]. Water polluted with heavy metals as Cd, Cu and Co ions has the most harmful effect in environment owing to, toxicity, long biological half life, aggregation in many body parts and carcinogenic nature [12-14]. These organic pollutants mostly existing as trace quantities which could accumulate through food chain and lead to serious health and environmental problems [15-17]. Hence, there are many efforts to invent a good approach for heavy metal removal from leftover water [18]. For example, membrane separation [19], chemical precipitation [20], coagulation and ions exchange [21] and adsorption [22]. Adsorption is considered as the most effective techniques for heavy metal removing from waste water [23], because of its low price, simple operation, easy regeneration and wide application [24]. Now, there are many scientists give their attention on the adsorbents have good ability for Cd (II) adsorption, such as metal oxides, activated carbon and chitosan. One of the most efficient materials for adsorption is considered to be metal oxides as, TiO$_2$, ZnO and Fe$_2$O$_3$ have paying great attention attributable to O- vacancy, good stability and low toxicity [25]. Among these metal oxides ZnO nanoparticles has been used as adsorbent of heavy metals ions due to low cost, non-toxicity, chemical and thermal stability and easy preparation [26-27]. Removal efficiency of ZnO can be enhanced by adding reduced graphene oxides [28]. Because of its large specific surface area, has large number of oxygenated function groups which is useful for adsorption process and well dispersed in aqueous solutions [29-30]. Herein, we prepared ZnO nanoparticles as well as ZnO-rGO nanocomposite by
using Alovera plant extract. Furthermore, the adsorption of Cd (II) has been tested on surface of ZnO and ZnO-rGO nanocomposite at different experimental parameters as pH value and contact time. Which enable us to determine the optimum condition for purification waste water from Cd(II). Moreover, adsorption isotherm and kinetics models were studied.

2. Experimental techniques

2.1 Synthesis of the materials

All chemicals are purchased from Sigma Aldrich with purity exceeds 98 % and use as received.

2.1.1 Preparation of graphene oxide GO by Hummer’s method.

The steps of preparation of graphene oxide from graphite using Hummer’s method are illustrated in our pervious work [1-5]. Briefly, First step [low temperature stage 0-5 °C] where graphite and concentrated H₂SO₄ acid are used as intercalating agent, step 2 [Medium temperature stage 35 °C] where KMnO₄ are used as oxidizing agent. Finally H₂O₂ and D.I water are uses for exfoliation assistant of the GO layers.

2.1.2 Preparation of Aloe Vera plant extract and reduced graphene oxide

The obtained Aloevera leaves were thoroughly washed with water to eliminate dust and contaminated contents and dried at room temperature. 100 gm of Aloe vera gel was taken and the gel extracted was collected and mixed well with water (150 ml) and continuously stirred at 60 C for 20 min. The solution was then cooled down and the resulting product was the leaf extract of Aloevera plant. It will add to graphene oxide solution to reduce it to reduced graphene oxide.

To prepare reduced graphene oxide 0.1 gm of graphene oxide is added to the 100 ml Alovera solution at 60 C for 15 min then sonication for 30 min.

2.1.3 Preparation of ZnO nanoparticles and ZnO -rGO nanocomposite

The preparation occurs by adding 0.3 M of Zink nitrate to 100 ml distilled water it will be equivalent to 8.9 gm, keep stirring for 15 min then increase the temperature to 60 C while adding drops of 0.1 M of NaOH. Let precipitate filter and dry. A white precipitate of ZnO nanoparticles is formed
ZnO-rGO nanocomposite is prepared by adding the reduced graphene oxide with Alovera plant extract to ZnO nanoparticles drop wise at 60 C under constant stirring, then sonicate for 60 min. Let precipitate, wash and dry the resultant grey powder and formation of ZnO-rGO nanocomposite is confirmed by characterization tools XRD, FTIR, FESEM, TEM as will be discussed below.

2.2. Adsorption study of prepared nano ZnO and ZnO-rGO nanocomposites

The adsorption performance of ZnO and ZnO-rGO nanocomposites was studied by batch sorption experiment. Initially, standard solution of heavy metal ion was prepared by dissolving 2000mg/l of Cd (NO3)2 in distilled water under vigorous shaking by using electric shaker (ORBITAL SHAKER SO1). The adsorption of Cd(II) by using prepared nanoparticles is tuned by experimental parameters as solution pH and contact time. To study the effect of pH solution, dissolving 0.02g of prepared sample in 10ml of standard solution. The pH of solution should adjust at different values (2-8) by using 0.1M nitric acid and ammonium hydroxide solution. After an hour, the solution is collected and filtrated for measuring concentration of heavy metal after adsorption process by using ICP spectroscopy. After perceptive the most favorable pH value for adsorption (i.e 6). Likewise, the optimum contact time can be fine-tuning, through dissolving 0.1g of prepared samples in 100ml of standard solution. The heavy metal (Cd(II)) concentration is measured after different time (10-120min). the removal efficiency of Zno and ZnO-rGO nanocomposite was considered by the following equation [1]
**Removal (adsorption) efficiency**

\[ \text{Removal (adsorption) efficiency\%} = \frac{C_0 - C_F}{C_0} \times 100\% \]  

Where:

- **C₀**: initial concentration of heavy metal soln (ppm)
- **Cₖ**: final concentration of heavy metal soln (ppm)

2.3 Characterization

The X-ray powder diffraction (XRD) data are collected using a computer controlled Bruker (D 8 discover) diffractometer with CuKα radiation \( k = 1.54056 \) Å. The measuring range from 5º to 100º and the instrumental resolution was 0.004– 0.005º. Data collected in step-scan mode with steps of 0.02º. Morphology of the produced materials by using a scanning electron microscope (SEM) model number JSM 6510 LV JEOL and transmission electron microscope (TEM) model number JEM 2100 JEOL. The atomic force microscopy (AFM) was obtained on AFM-Agilent Technologies.

3. Results and discussion

3.1 Structural Characterization

The XRD of GO and ZnO-rGO are shown in Figure 2.a and 2.b. GO exhibited a strong peak at \( 2\theta = 11.01° \), indicating that d-spacing of GO (001) is approximately 8.03 Å according to the Bragg equation. The d-spacing of GO is much larger than that of graphite (3.4 Å) which is attributed to the introduction of oxygen-containing functional groups (C-OH, C=O, COOH) on the surface of GO, in which facilitate the hydration and exfoliation of GO sheets in aqueous media. In XRD patterns of ZnO–rGO nanocomposite, The beaks of ZnO are clearly seen sharp and broad with hkl identified as shown in Fig. 2.b. the main diffraction peaks can be assigned to the hexagonal structure, space group P 63 m c (186) (COD 2300113). Unlike the X-ray pattern of Graphene oxide, the nanocomposite of ZnO-rGO doesn’t show any peak at \( 2\theta = 11° \) in the XRD pattern. This may attributed to the oxygen-containing groups of GO are removed and GO are reduced to graphene oxide rGO by the Aloveraplant extract. The diffraction peak of rGO which is usually observed at \( 2\theta = 24° \) (002)
usually weak and very broad due to lack of crystallinity of graphene. In the XRD patterns of the ZnO-rGO (002) usually doesn’t appear due to the diffraction peaks of nanocrystals ZnO are much stronger than (002) of rGO and its marked by arrow in Fig.2.b

Fig. 2.a XRD pattern of graphene oxide GO

Fig.2.b. XRD pattern of ZnO-rGO nanocomposite

The FTIR spectra measured from 4000-400 cm\(^{-1}\) using compressed ballet of KBr. The peaks around 3400-3500 cm\(^{-1}\) are vibration of OH due moisture. FT-IR spectra of GO, ZnO-rGO nanocomposites are shown in Fig. 3. In the transmission curve of
GO, the characteristic peaks at 3430 and 1710 cm\(^{-1}\) correspond to the stretching vibrations of O–H and C=O bands. The stretching peak of C–C at 1052 cm\(^{-1}\) and the vibration peak of C=C at 1618 cm\(^{-1}\). For the ZnO-rGO, the characteristic vibration peaks around 575 cm\(^{-1}\) is assigned to the stretching mode of the Zn–O. The peak at 1600 cm\(^{-1}\) corresponds to C=C is exists and indicating the existence of graphene nanosheet [2, 5]. The results of FT-IR spectra are verifying that the ZnO-rGO nanocomposite is formed in the synthesis.

Fig. 3 FTIR spectra of GO and ZnO-rGO nanocomposite

### 3.2 Morphological Characterization

The SEM images are shown in Fig. (4: a, b) confirm the formation the material in nanoscale the average crystallite size is about 70 nm. Figure 4. c show the AFM of ZnO-rGO nanocomposite. The analysis of these protrusions results showed a distribution of Zmax and Zmin to be 109 nm and 40 nm, respectively, and the mean is around 70 nm. The TEM images are shown in Fig. 4. (d, e, f) the graphene sheets
appears as wrinkled paper while the nanorod crystal of ZnO is attached and distributed on the surface.

Fig. (4:a,b): SEM images of ZnO - rGO nanocomposite

Fig. 4: AFM of ZnO-rGO nanocomposite

3.3 Activity in water treatment
The uptake behavior of Cd (II) ions by ZnO and ZnO-rGO was investigated at different experimental parameters as pH as well as contact time. **Fig. (5)** shows the effect of pH solution on adsorption behavior. It is clearly that Zno and ZnO-rGO follow same trend which is as pH increased, the adsorption of Cd(II) ion increased. The lower adsorption of heavy metal at lower pH value is related to competition between H\(^+\) and Cd\(^{2+}\) over the available active sites of adsorbent [31]. As pH value increased up to 6 H\(^+\) decreased and more active sites become available for Cd (II) adsorption [32]. Otherwise, at basic pH (i.e. 8), oH\(^-\) ions exist in solution. Consequently, Cd (oH)\(^2\) is formed [33]. So, Cd(II) ions were removed by adsorption in addition to precipitation. For that reason, the optimal pH was preferred to be 6.

**Fig. (5):** Removal efficiency % of Cd(II) as a function of pH solution by using ZnO and ZnO-rGO

Another parameter has a durable effect on adsorption of heavy metal ions is contact time. **Fig. (6)** displays the relation between removal efficiency of Cd(II) ions by using
ZnO and ZnO-rGO nanocomposite at different contact time over range (10-120) min.

Fig. (6). Relation between removal efficiency % of Cd(II) by using ZnO and ZnO-rGO nanocomposite and contact time.

It is obviously that, there is continuous rise in adsorption with increasing contact time till reach to equilibrium after 80 and 90 min for ZnO and ZnO-rGO nanocomposite respectively. Rapid adsorption at the beginning due to availability of large no of active sites [34]. Removal of Cd(II) by using ZnO was reached equilibrium before ZnO-rGO nanocomposite can be related to number of available active sites in ZnO surface is less than that in ZnO-rGO nanocomposite has. Removing efficiency Performance of ZnO-rGO is preferred than ZnO. As it reached to 90% after 90min. this can be explained by unique structure and great oxygen number–covering functional groups on GO surface, make it fine dispersed in water [35]. Finally, the
optimum conditions for adsorption of Cd(II) are pH 6 for 90 min by using Zno-rGO nanocomposite.

Studying adsorption isotherm as well as kinetics is the only way for discovering the mechanisms followed in adsorption process [36]. There are two isotherms used to explain the adsorption which are Langmuir and freundlish isotherms. Langmuir as well as Freundlish isothermers are expressed through equation (2) and (3) respectively.

\[
\frac{C_e}{q_e} = \frac{1}{k_l q_m} + \frac{C_e}{q_m} \quad (2)
\]

\[
\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (3)
\]

where \(q_e\) and \(q_m\) (mg g\(^{-1}\)) are the adsorption capacity at equilibrium and maximum adsorption respectively, and \(K_l\) (L mg\(^{-1}\)) is the affinity binding constant. while \(K_f\) and \(n\) are physical constants signifying the adsorption capacity and intensity of adsorption, respectively.

The Langmuir isotherm is related to monolayer adsorption at homogeneous sites and equivalent adsorption energies [37]. While, Freundlish isotherm is described heterogeneous surfaces [38]. By fitting Fig (7:a,b) we found that, langumir model is more fit and from another hand, the correlation coefficient (R\(^2\)) for freundlish (0.83667) is relatively smaller than that for Langmuir (0.94009). Therefor, adsorption of Cd(II) on surface of prepared sample occurred through monolayer adsorption and

![](image)

Fig. (7:a,b). Langmuir and Freundlish isotherm.
Heavy metal adsorption kinetics are often studied by using pseudo first order and pseudo second order kinetics. Pseudo first order kinetics describes the physisorption. Physisorption is weak occurs without chemical bonding, only vander waals forces exist. Consequently, this adsorption is considered to be reversible. While the pseudo-second order kinetic deals with chemisorption adsorption which is occurred through two reactions. The first reaction, it extents equilibrium quickly, while the second leaks slowly and reach equilibrium after long time [38]. In chemisorption, there is bond formation between adsorbates and adsorbents through electron sharing. So, it is stronger than physisorption. Another type of kinetic models is the intra particle diffusion kinetic model. Weber and Morris model is studying this type of kinetic. Which accepts that, intra particle diffusion model is the single rate –determining stage, meanwhile, the mass removal of adsorbate is well-thought-out a rapid process [39,40].

To explain the adsorption kinetic mechanism, three models of kinetics were studied:

Pseudo first-order model: \[
\ln(q_e - q_t) = \ln q_e - \frac{k_1}{2.303} t 
\] \hspace{1cm} (4)

Pseudo second-order model: \[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \hspace{1cm} (5)
\]

Inter particle diffusion model \[
q_t = k_3 t^\frac{1}{2} + C \hspace{1cm} (6)
\]

Where:

\( k_1 \) is the pseudo first,

\( k_2 \) is the pseudo second-order,

\( k_3 \) is the inter particle diffusion rate constants.
Fig. (8): Pseudo-first-order model for the adsorption of Cd(II) at Zn-rGO nanocomposites.

Fig. (9): Pseudo-second-order model for the adsorption of Cd(II) at Zn@Go nanocomposites.
It can be decided that, furthermost of heavy metal ions adsorption on surface of ZnO-rGO nanocomposites had close-fitting with the pseudo-second order kinetic model, refereeing to the fig. (8:9) as well as the correlation coefficient which have values (0.826, 0.9820 and 0.9630) for pseudo first order, pseudo second order and intra particle kinetic models respectively.

**Conclusion**

ZnO and ZnO-rGO nanocomposite were prepared successfully by simple green synthesis method using Alovera plant extract. The characterization tools (XRD, FTIR, SEM, TEM, AFM) proves the correct synthesis. The prepared samples used as adsorbent for heavy metal ions (Cd(II)). The removal efficiency were increased from 80% to 90% by adding rGO to ZnO. The optimum conditions for adsorption of Cd(II) achived at pH6 after 90 min and by using ZnO-rGO nanocomposite. For isotherm and
kinetics studied, we conclude that the adsorption of Cd(II) on the surface of prepared nano samples occurred through monolayer adsorption described by langumir model by chemisorption reaction as it is, follow pseudo-second order isotherm.

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