



EXPERIMENTAL STUDIES ON CHARACTERIZATION OF SYNTHESIZED GRAPHENE OXIDE NANOPARTICLES & IT'S APPLICATION

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Abstract:

Phosphates present in wastewater effluents cause health hazards like headache, weakness, dizziness, kidney damage etc., In order to reduce the phosphates in the wastewater few removal methods like electrocoagulation, adsorption are included. In the present study Graphene Oxide nano particles (GONP) were used to remove phosphates from synthetic or aqueous solution. The characterization of Graphene Oxide nanoparticles were studied using FTIR, SEM and XRD. The maximum GONP removal rate was 92.32% in the experimental process by optimizing the parameters like contact time (40min), dosage of adsorbent (0.3g/L), pH (7), Initial Concentration of aqueous phosphate solution (50ppm) and Temperature (318K) in arrange to attain the adsorption efficiency. The adsorption kinetics were examined and displayed by first and second order rate in this study.

Keywords: Graphene Oxide Nanoparticles; Phosphate; Adsorption; FTIR; X-Ray Diffraction.

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1. Introduction

The Phosphates found in eutrophication of water have numerous harmful effect. It destroys the amphibious life and degrades water quality. Phosphate removal methods are adsorption, chemical precipitation, membrane separation, electrocoagulation, ion exchange, crystallization are included. Adsorption is used mainly with less cost and more efficient processes [1]–[4]. Graphene Oxide (GO) has been oxidized to scramble the carbon layer with atoms of oxygen after that diminished to totally isolated the carbon layer into one or more graphene covers. GO is even byproduct of the oxidation because when the oxidizing agent reacts with graphite, the distance between the graphite layer increased [5], [6]. Several studies have concentrated on adsorbent modifications such as graphene [3]. Others have done it on functionalized graphene oxide with silver nanoparticles [7], a nanocomposite of graphene oxide magnetic strontium [8] and various composites on graphene [9]. The graphene based material showed good phosphate removal efficiency. In this consider, the phosphate adsorption properties of GONP was explored in different variables like time, temperature, dose, concentration of phosphates & pH. Kinetics, Isotherms and thermodynamic studies were calculated from experimental values.

2. Materials and Methods

2.1. Material

HCl, Sulphuric acid, NaOH, Na_2HPO_4 , NaNO_3 , Ammonium Molybdate, Ascorbic Acid, Potassium Permanganate, Sodium nitrate, graphite powder.

2.2. Equipments

UV spectroscopy, Heating Incubator, pH meter, Micro Pipette, Glass ware like beakers, conical flasks, measuring jar, Volumetric flasks etc.

2.3. Synthesis of GONPs

1 gm of fine graphite powder in a conical flask and add 1 gm of NaNO_3 & 50 ml of Sulphuric acid put into an ice bath and maintain a temperature of around 20°C – 25°C with stirring for 4hrs. After completion of stirring, 4 gm of KMnO_4 is added and mixed well with respect to maintain the temperature. After addition of KMnO_4 , it is heated to 35°C blend for 2hrs. Add 100 ml of DI water and heated up to 95°C for well mixing and cool to atmospheric. The mixture were used 10 milliliter of H_2O_2 . Mixture is washed with 10% of HCl and DI water to purify the sample. After filtration, it can be dried at room temperature and it is in powder form [10], [11].

2.4. Determination of Phosphates

Phosphates is determined by color using UV Spectroscopy. 10ml sample of aqueous phosphate solution was taken in test tube and add $600\mu\text{l}$ of Ammonium molybdate & $200\mu\text{l}$ of Ascorbic acid. Initially aq. Phosphate is a colorless solution, after adding an ammonium molybdate and ascorbic acid colorless change to blue color with in 5mins. [12].

2.5. Experiment - Removal of phosphates

0.15g of Na_2HPO_4 was diluted in sample into a 1 liter of distilled water in volumetric flask. Take 50ml of aqueous phosphate solution and 10mg adsorbent dosage was added in each conical flask. Then kept the solution without any disturbance. Collect the test for each five minutes and watched optical density of aqueous phosphate solution using UV Spectroscopy & notice percentage removal with increase in time. After equilibrium time reached, time increases removal percentage is remains constant. Similar to other parameter of adsorbent dosage was 50ml of aqueous phosphate solution in each conical flask with different dosages when time parameter was fixed earlier. Similar to pH parameter by varying pH natures of acidic, basic and neutral. And also, the other parameters like Initial concentration of phosphate and temperature by varying the ppm's and temperature with equilibrium/constant parameters of time, adsorbent dosage and pH [13]–[16].

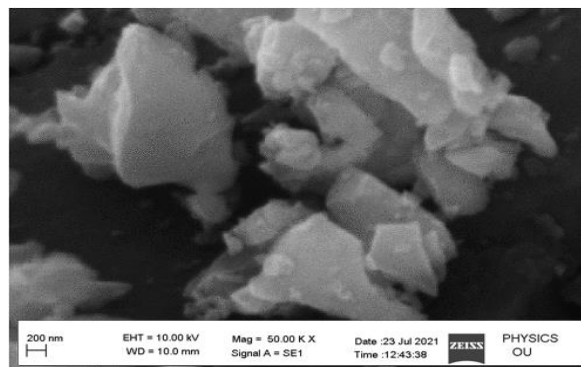


Fig. 1. GO of SEM

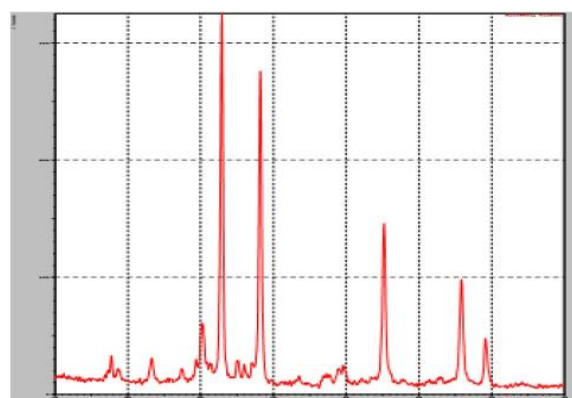


Fig. 2. GO of XRD

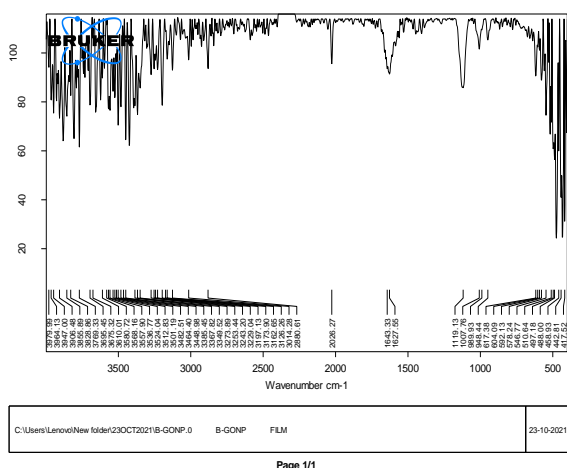


Fig. 3. a) FTIR spectra before analysis of GONP

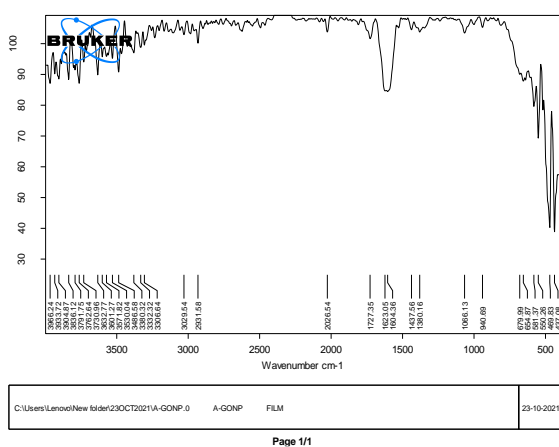


Fig. 3 b) FTIR spectra after analysis of GONP

2.6. Characterization of GONPs

SEM was utilized to recognize the molecule estimate by filtering the surface with a centered bar of electrons association with molecules in GONPs. SEM picture of GONP appeared in Fig. 1 distinctly mention the tiny shape and various dimensions of GONP.

XRD was based on wave-particle duality properties and it gives about crystalline material structure. The technique is mainly used to recognize and characterize of compounds by various design. GONP has the irregular structure and the peak positions in Fig. 2 show the arrangement of the identical. The crest at 2θ values of 34° , 37° , 55° , 66° and 69° . comparing grid focus with favored introductions which are has a place to most ground crest (0 0 2) and (0 1 0) plane. [17], [18].

3. Result & Discussions

3.1. GONPs analysis -FTIR

Fig. 3a & 3b represents the FTIR range of GONP. The wide crest at $4000 - 3000 \text{ cm}^{-1}$, in higher vitality locale and crest within the lower extend at $1007 - 948 \text{ cm}^{-1}$ was due to O – H extending and

O – H bending individually. C – O extending vibration at 1119 and 1066 cm^{-1} were ascribed to polyphenolic compounds and hydrocarbon. GONP stretching of nanoparticles is within the extend of $546 - 417 \text{ cm}^{-1}$. All other crests are characterizing arranged GONP. After adsorption, crests moved to lower wavenumbers and had clearly weakened. Particularly, the trend for crests to diminishes as appeared in figures [19].

3.2. Variables of Effect

3.2.1. Time effect

200 mg/L of GONP was taken in each conical flask. The stock arrangement of phosphates with 100 ppm concentration was arranged and time course profiles for the adsorption of phosphate solutions onto utilized GONP appeared time 40 mins was needed to realize an equilibrium adsorption and there was no critical alter in conc. of PO_4^{3-} . Fig. 4. Shows increased contact time with increase in % removal of phosphates. For a given initial concentration, the amount of phosphate and adsorbent were known. phosphates were occupied in the adsorption sites for certain time and repelled the phosphates in solution when equilibrium time was reached.

3.2.2. Adsorbent dose effect

For examining an impact on adsorbent dose of expulsion of phosphates, adsorbent is changed from 0.1 to 0.6 g/L , settling other parameters steady. The time has 40 mins for GONPs. Fig. 5 appears an increment in rate 80.15 to 87.02 for 100 ppm phosphate solution with an increment of adsorbent dose from 0.1 to 0.6 g/L , the increment in aq. removal of phosphate with adsorbent dose will expanded surface region.

3.2.3. pH effect

The pH of aq. solution as balanced by including required amount of 0.1 N NaOH and 0.1 N HCl . The pH effect on aqueous phosphate solution by switching pH was set to $2, 4, 6, 7, 8$ and 10 in each of the conical flask and constant other variables are time 40 mins , adsorbent dose 300 mg/L . By increasing the pH, percentage removal of phosphate increments up to pH 7 and decrease to pH 11 . When pH is lower, the surface of GONPs is positively charged which makes the surface suitable for anions. At high pH, the oxide surface incorporates a net negative charge and tends to repel anionic phosphates in solution. The most elevated removal % is takes place at pH 7 as appeared in Fig. 6.

3.2.4. Conc. of phosphates effect

To study the effect of conc. on removal of phosphates by switching the conc. on removal of phosphates by switching the conc. of 50 - 300 ppm and fix remaining variables are time 40mins, adsorbent dose 0.3g/L, pH-7. As the conc. of phosphates increases, the active sites required for the adsorption of phosphates will not sufficient to occupied for the increasing amount of phosphates in solution, and the removal percentage decrease and q_e increases. The most elevated removal percentage at 50 ppm as appeared in Fig. 7

3.2.5. Temperature effect

The temperature from 303K to 318K by increasing 5°C and fix remaining variables are time 40mins, adsorbent dose 0.3g/L, pH is 7 and different concentrations from 50 to 200ppm. As the Temperature increases, removal percentage also increases at 318K as shown in Fig. 8.

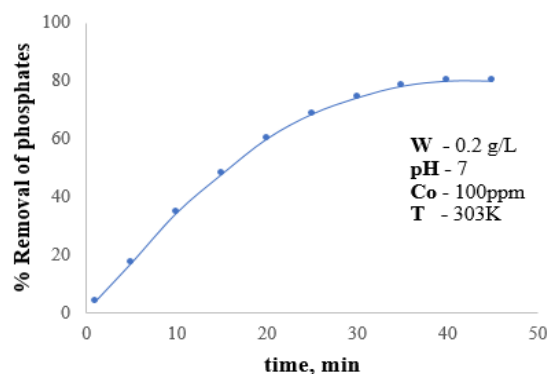


Fig. 4. Effect of Contact time on % Removal of Phosphates

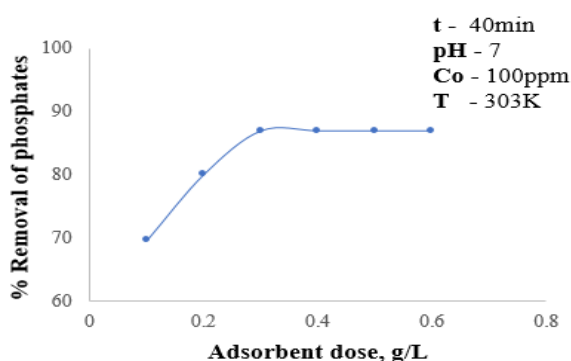


Fig. 5. Effect of Adsorbent dosage on % Removal of Phosphates

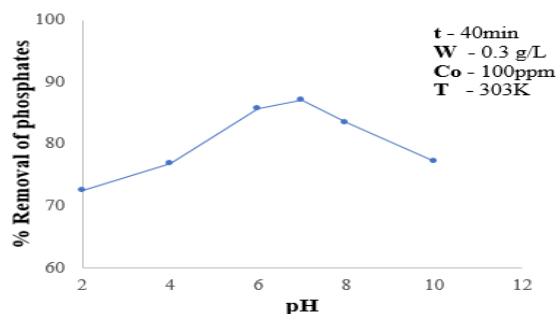


Fig. 6. Effect of pH on % Removal of Phosphates

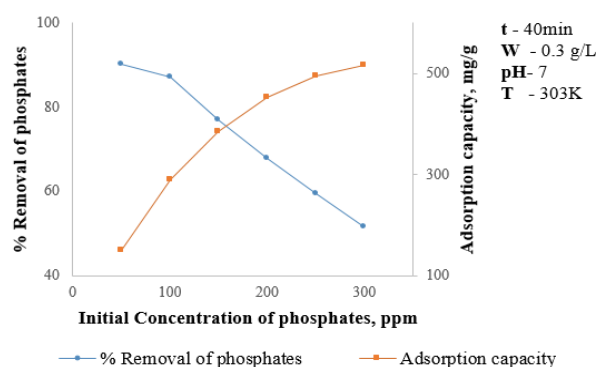


Fig. 7. Effect of Conc. of phosphates on % Removal of Phosphates

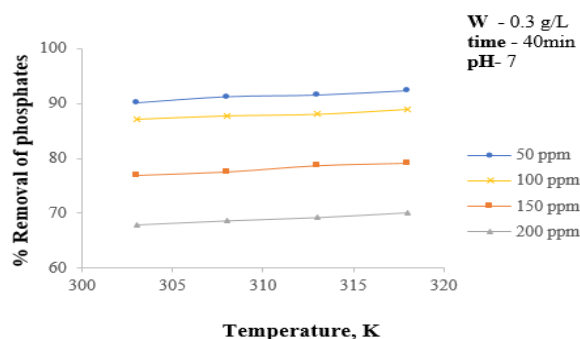


Fig. 8. Effect of Temperature on % Removal of Phosphates

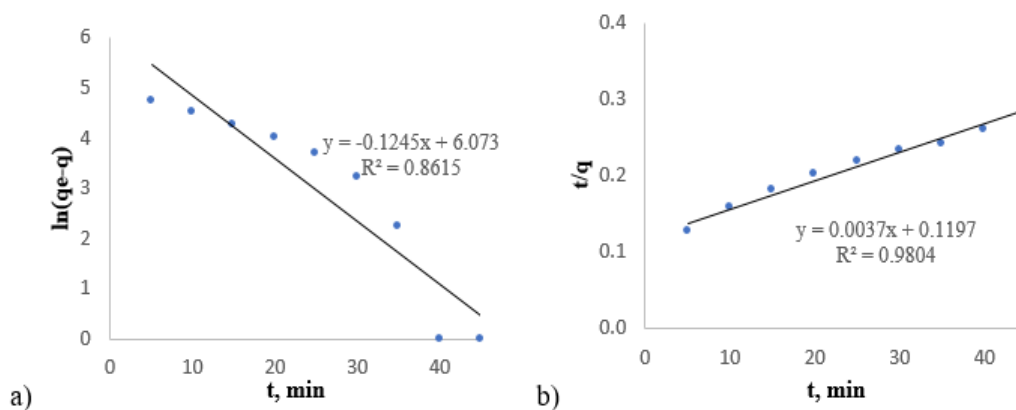


Fig. 9. a) Pseudo 1st order b) Pseudo 2nd order

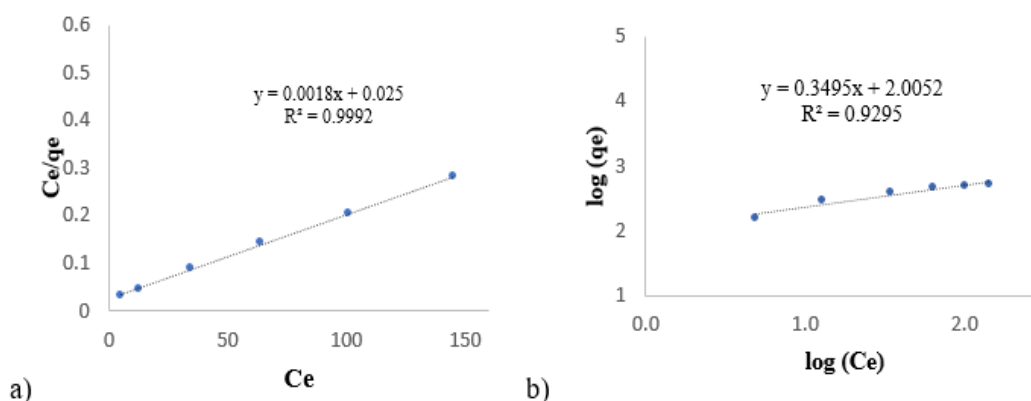


Fig. 10. a) Langmuir Isotherm b) Freundlich Isotherm

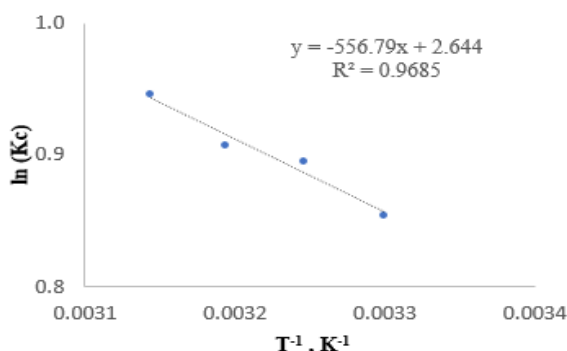


Fig. 11. $\ln K_c$ vs T^{-1}

3.3. Kinetics

3.3.1. Pseudo 1st Order

It is generally expressed as ,

$$\frac{dq}{dt} = k_1 (q_e - q) \quad (1)$$

$$\Rightarrow \ln(q_e - q) = -k_1 t + \ln q_e \quad (2)$$

From eq (1) gets integrated with limits and got an eq (2). Analyzing the experimental data, from Fig 9a, using eq (2) Plot $\ln(q_e - q)$ vs t shows a linear relationship from which slope and intercept of the k_1 and q_e values can be determined. The calculated results were shown in Table 1. It is concluded that the pseudo 1st order model was not fitted well.

3.3.2. Pseudo 2nd Order

It is generally expressed as ,

$$\frac{dq}{dt} = k_2 (q_e - q)^2 \quad (3)$$

$$\Rightarrow \frac{t}{q} = \left(\frac{1}{q_e}\right)t + \left(\frac{1}{k_2 q_e^2}\right) \quad (4)$$

From eq (3) gets integrated with limits and got an eq (4). Analyzing the experimental data, from Fig 9b, Plot t/q vs t shows a linear relationship from which slope and intercept of the q_e and k_2 values can be determined. The results were shown in Table 1. It is suggested that pseudo 2nd order kinetics is the best fit for this information [20].

3.4. Isotherms

3.4.1. Langmuir

Generally expressed as,

$$\frac{C_e}{q_e} = \left(\frac{1}{q_{max}}\right)C_e + \left(\frac{1}{q_{max} k_l}\right) \quad (5)$$

Analyzing the experimental data, from Fig. 10a, Plot C_e/q_e vs C_e shows a linear relationship from which slope and intercept of the q_{max} and k_l values can be determined. The highest R^2 confirms good

act for the phosphate of equilibrium adsorption to nano graphene oxide at various temperature. Langmuir isotherm at 303K was found to be 555.55mg.g⁻¹ [21, 22] and the adsorption intensity, k_1 is 0.072L/mg.

3.4.2. Freundlich

It can be generalized as

$$\log q_e = n \log C_e + \log k_f \quad (6)$$

Where k_f is Freundlich constant and n is intensity of adsorption

Analyzing the experimental data, from Fig. 10b, Plot $\log q_e$ vs $\log C_e$ shows a linear relationship from which slope and intercept of the n and k_f values can be determined. However, the value of regression is lower than the Langmuir isotherm [23].

Table 1. Kinetic studies at optimized conditions

Pseudo order	q_e (exp)	50 mg L ⁻¹ at 318K q_e (cal)	k	R2
First order	153.87	433.98	0.1245	0.8615
Second order	153.87	270.27	1.14x10 ⁻⁴	0.9804

Table 2. Thermodynamic parameters for the adsorption of phosphate

T/K	K_c	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
303	2.234	-2.02		
308	2.326	-2.16		
313	2.357	-2.23	4.63	21.98
315	2.449	-2.36		

3.5. Thermodynamic studies

Phosphate adsorption on nano graphene oxide was estimated by thermodynamic variables of ΔG° , ΔH° and ΔS° .

$$\Delta G^\circ = -R T \ln K_c \quad (7)$$

$$\Rightarrow \ln K_c = \left(-\frac{\Delta H^\circ}{R} \right) * \left(\frac{1}{T} \right) + \left(\frac{\Delta S^\circ}{R} \right) \quad (8)$$

Where; universal gas constant is R , T is temperature in K, equilibrium constant is K_c .

Analyzing the experimental data, from Fig. 11, using Van 't Hoff equation using eq (8), Plot $\ln k_c$ vs $1/T$ shows a linear relationship from which slope (ΔH°) and intercept (ΔS°) values can be presented in Table 2. The negative value of ΔG° indicates that the phosphate adsorbed spontaneously to the adsorbent. A positive value of ΔH° indicates that the endothermic nature of adsorption process. A positive value of ΔS° indicates that the randomness of the solution interface increases during phosphate

GO at high temperatures may be due to the expansion of pores size on the surface of the adsorbent [24].

4. Conclusion

Experimental data was obtained for removal of phosphate using GONP as adsorbent. The various effects of adsorption process such as time, temperature, adsorbent dose, concentration and pH. The kinetics of the adsorption of phosphates on GONP can be better described with 2nd order kinetics. The Langmuir and Freundlich isotherm for phosphate proved to be the best adjustment of experimental data for GONP. The thermodynamic variables such as of ΔG° , ΔH° and ΔS° are calculated and the adsorption process is endothermic in nature.

Conflicts of interest

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of this article.

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