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Efficient Use Of Graphene Nano Platelets For Removal Of Antibiotic Drug From Aqueous Solution

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Abstract:*The analytical study of the Metronidazole antibiotic drug (MNAD) was carried out through its spectrophotometric method of determination followed by its removal from aqueous solution using magnetically modified graphene nanoplatelets (MMGN). The MMGNs were prepared by mixing GNPs with freshly prepared magnetite nanoparticles and the new characteristics were further observed during the investigation. The homogenous distribution of the magnetite nanoparticles over the transparent platelet-like graphene platelets were revealed as output in the result. The results showed that the MMGNs have superior adsorption capacity compared with the pristine GNPs and the magnetite nanoparticles. The effect of different operational parameters which affect the removal process were explored such as; adsorbent amounts, contact time, initial pH, temperature, and the initial concentration of MNAD. The results showed the great affinity of the MMGNs towards the MNAD and the maximum adsorption capacity was found to be 102.56 mg g-1. The adsorption mechanism of MNAD by the MMGNs involved π-π stacking and electrostatic interaction. The adsorption was studied both kinetically and thermodynamically and mainly was found to follow pseudo-second-order kinetic model as well as it was spontaneous and exothermic in nature. The MMGNs exhibited a great adsorption ability to remove MNAD from the model aqueous solution.*

Keywords*: Metronidazole (**MN**AD), MMGNs**, Adsorption; Antibiotic drug; Graphene; Kinetics; Magnetic separation, Thermodyanmics, Aquatic/Water Pollution*

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I. Introduction

Water pollution is a serious threat for human health, ecosystem and in terms of depletion of clean water resources. Water pollution is considered as one of the most sensitive problem emerging in the 21st era . One of the sources that causes water pollution, even in small concentrations, are the pharmaceuticals , as about 70–90% of the given dose can remain non-degradable in the human or animal body, and is largely excreted as an active compound. Pharmaceutical residues have adverse effects towards non-target organisms. Especially release of antibiotics to the environment causes enhanced resistant bacteria, therefore the removal of the antibiotics from waste water is very important to protect the ecosystem. Metronidazole is an antibiotic of class nitroimmidazole which works by stopping the growth of bacteria and protozoa and only treats bacterial & protozoal infections. As it fights bacteria in our body, it is used to treat bacterial infections of the stomach, skin joints and respiratory tract. Metronidazole consumption is higher than the other types in the nitroimmidazole class because of the oral absorption ability, and unfortunately, it is non-biodegradable and also an inhibitor of the photosynthesis mechanism of algae species. Nowdays Nanotechnology is currently retrieving a big deal of work due to their high surface area, small particle size, great potential, great intrinsic reactivity and capabilities as a catalytic reagent of a pollutant through changing reaction mechanism. Nanoparticles have been widely used for the environmental applications because of its high efficiency in variety of pollutants including organic compounds, inorganic compounds, pharmaceutical compounds, chlorinated compounds and nitro-groups respectively. The high reactivity of the magnetic Nanoparticles for pollutant removal, a compact and efficient wastewater treatment system and also it is expected that magnetic separation could be a more cost effective and conventional method for separating such tiny particles than sophisticated membrane filteration of magnetic nanoparticles .

About the Antibiotic drug:

Metronidazole,USP is chemically designated 2-methyl-5-nitroimidazole-1-ethanol ($C_6H_9N_3O_3$), a crystalline powder sparingly soluble in water. The metabolites of metronidazole result primarily from side-chain oxidation [1-(βhydroxyethyl)-2hydroxymethyl-5-nitroimidazole and 2-methyl-5-nitroimidazole-1-ylacetic acid] and glucuronide conjugation. Both the parent compound and the hydroxyl metabolite possess in vitro

antimicrobial activity. Metronidazole is the major component found in the plasma with lesser quantities of metabolites also being present.

Mechanism of Action:

Metronidazole, a nitroimidazole, exerts antibacterial effects in an anaerobic environment against most obligate anaerobes. Once metronidazole enters the organism by passive diffusion and activated in the cytoplasm of susceptible anaerobic bacteria, it is reduced; this process includes intra-cellular electron transport proteins such as ferredoxin, transfer of an electron to the nitro group of the metronidazole, and formation of a short-lived nitroso free radical. Because of this alteration of the metronidazole molecule, a concentration gradient is created and maintained which promotes the drug's intracellular transport.

II. Methodology:

Materials Required:

Graphene Nanoplatelets with thickness ranging from 1 to 20 nm, $FeCl_3 \cdot 6H_2O$, $Fe(SO_4) \cdot 7H_2O$, HCl, ammonia solution (Merck, 25 %), Metronidazole antibiotic drug (MNAD), 8M NH_4OH, 0.1 M NaOH, 0.1 M H_2SO_4, 1-10 Phenanthroline, Sodium acetate, giacial acetic acid, Hydroxylamine Hydrochloride, Ferrous ammonium Sulfate (FAS),

Apparatus used: UV-Visible Double Beam Spectrophotometer (Systronics),

Graphene Nanoplatelets are unique nanoparticles consisting of short stacks of graphene sheets having a platelet shape with thickness ranging from 1 to 20 nm and width ranging from 1 to 50 μm. $FeCl_3 \cdot 6H_2O$, $Fe(SO_4) \cdot 7H_2O$, HCl, and ammonia solution (Merck, 25 %) was used in the synthesis of magnetite (Fe_3O_4). Metronidazole was obtained & purchased. All the reagents employed in the experiments were used without further purification. A stock solution of 1000 mg/l containing drug was prepared, and dilution was performed for the calibration solutions and adsoption study solutions.

Synthesis of magnetically modified graphene nanoplatelets (MMGNs)

200 ml aqueous solutions of graphene nanoplatelets (GNPs) was prepared. The aqueous solution in the molar ratio of $Fe^{2+}:Fe^{3+} = 1:2$ was prepared and a few drops of concentrated HCl were added for complete dissolution of iron salts. It is then added to the graphene solution and the mixture was kept for 10 minutes. The mass ratio of graphene:Fe_3O_4 was adjusted to be 75:25. Solution of 8M NH_4OH was added drop wise till the pH reaches 11–12. Finally, the mixture was kept at 50°C under mechanical stirring. The precipitation was magnetically separated from the aqueous phase and the composites were washed with deionized water and ethanol, further it was dried at 60°C in vacuum oven.

Adsorption Studies

The adsorption experiments were carried out in batch mode by mixing a specific amount of adsorbent and 10 mL of antibiotic solution in the stoppered conical flask under constant shaking (120 rpm) in a thermostat shaker. The effects of contact time, amount of adsorbent, initial drug concentration, pH, and temperature of the drug solutions were investigated. For determination of the equilibrium time of adsorption, the experiments were carried out specific time intervals. The adsorption conditions were chosen as nearly 5 mg of adsorbents and 10 mg/l antibiotic solution for determination of the effect of contact time. In the effect of amount of adsorbent experiments, 1-10 mg of adsorbents was used. For the effect of initial drug concentration experiments, the concentration range was chosen as 3-30 mg/l. To investigate the pH effect, 10 mg/l of drug solutions were prepared at pH 3, 7, 9 and 11. The 0.1 M NaOH and 0.1 M H_2SO_4 were used for pH adjusting. The temperature effect was investigated for three different temperatures, 20°C, 30°C, and 40°C. After the completion of the adsorption experiment, a magnet was brought to the side of the flask, which attract the entire magnetically modified graphene nanoplatelets and a clear solution was left behind. The clear solution was collected by a glass pasture pipette and the concentration of drug was measured. The drug concentration was followed by UV-Vis spectrophotometer at 230 nm. The uptakes of adsorbents (qe, mg/g) were calculated by the equation 1. C0 and Ce (mg/l) are initial concentration and equilibrium concentration of antibiotic drug, respectively; V (l) is the volume of the solution; m (g) is the amount of adsorbent. The removal efficiency was calculated further .

Equilibrium study

The adsorption isotherms mainly depend upon the equilibrium equations, which provide valuable information about the surface properties of the adsorbent by calculating the maximum adsorption capacity. Adsorption isotherms describe the relationship between the amount of adsorbate adsorbed by the adsorbent (qe) and the adsorbate concentration remaining in the solution after the system has attained the equilibrium state (Ce) at constant temperature. The adsorption of drug on MMGNs was analyzed using three different well-known equilibrium equations; Langmuir, Freundlich, and Temkin isotherm models, at three different temperatures; 293

K, 303 K, and 313 K, and the results are presented in the Figure provided. Langmuir isotherm model, which defines a monolayer adsorption, where Ce is the equilibrium concentration of adsorbates in the solution (mg L-1), qe is the uptake of the adsorbates (mg g-1), qm is the monolayer adsorption capacity of adsorbents for adsorption of adsorbates (mg g-1), and KL is the Langmuir adsorption equilibrium constant (L mg-1). Freundlich isotherm model is expressed where KF (L/mg) and n are the Freundlich constants. 1/n is defined as heterogeneity factor in this isotherm. Freundlich isotherm defines a heterogeneous adsorption with different surface energy sites and assumes the change of uptake with exponential distribution of adsorption sites and energies. Temkin isotherm model where KT=RT/bt, bt is the Temkin constant related to heat of sorption (J mol-1), f (L g-1) is the equilibrium binding constant corresponding to the maximum binding energy, R is the universal gas constant (8.314 J mol-1 K-1), T is the solution temperature (K). Temkin model is a proper model for the chemical adsorption based on strong electrostatic interaction between positive and negative charges. The parameters for each adsorption isotherm models were calculated. The average of the R2 values of the Langmuir and Temkin isotherm models are found approximately the same. Accordingly, the adsorption mechanism composed of both a monolayer adsorption and electrostatic interaction between the surface and the adsorbate through the π-π stacking, which agreed well with ionic strength investigation.

Kinetic study

The variation of the amount of antibiotic drug adsorbed by MMGNs at 293 K as a function of the adsorption time was studied and the experimental results were presented. The other experimental conditions was 9.5 mg L-1 antibiotic drug solution concentration, 5 mg adsorbent mass and pH=5. Adsorption was reached equilibrium in 90 min, no further improvement in adsorption % was observed, and the adsorption capacity reached 14.10 mg·g-1. Also, it was clear that antibiotic drug adsorption can be occured in two stages. The first stage was occured during the first 30 min of adsorption, and can be characterized by the high number of active binding sites on the MMNGs' surface during this phase. Adsorption can occur rapidly in this step, which indicate that the adsorption was controlled by the diffusion process of the antibiotic drug molecules from the bulk phase to the MMNGs' surface. In the second step, adsorption was most likely an attachment-controlled process due to the decrease in the number of active sites available for the antibiotic drug molecules on the GNPs' surface.

Result And Discussion

- Magnetically modified graphene nanoplatelets (MMGNs) were prepared
- MMGNs were used for the removal of antibiotic drug Metronidazole from model solution
- The effect of different parameters were explored that affected the removal process
- The adsorption was analyzed both kinetically and thermodynamically
- The results show that the MMGNs exhibited a great adsorption ability to remove Antibiotic drug Metronidazole from the model aquoues solution

III. Conclusion

Magnetically modified graphene nanoplatelets show the homogenous distribution of the magnetite nanopartilces within the graphene nanoplatelets. The adsorption behavior of antibiotic drug was investigated, by high surface area M-GNPs from aqueous solutions and the results showed that most of the Antibiotic drug was removed within 120 min using 9.8 mg adsorbent, at pH 5.0 and 293 K. Adsorption equilibrium data were fitted using both Langmuir and Temkin isotherms, and the Langmuir maximum adsorption capacity was found to be 112.48 mg g-1. Adsorption for Antibiotic drug was studied kinetically and thermodynamically, and found to be well fitted by the pseudo second order kinetic model, spontaneous and exothermic in nature. The adsorption behavior of Antibiotic drug on M-GNPs involved π-π stacking and electrostatic interaction, and the rate determining step was the π–π electron donor– acceptor interaction. Recovery, and reusability of the adsorbent was investigated, and the adsorbents showed great ability for the removal of Antibiotic drug for many times without losing its stability. Generally, M-GNPs could be considered a potential and promising adsorbent for the removal of organic pollutants from polluted water.

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Observation Table & Figures:

Table 1 Isotherm parameters

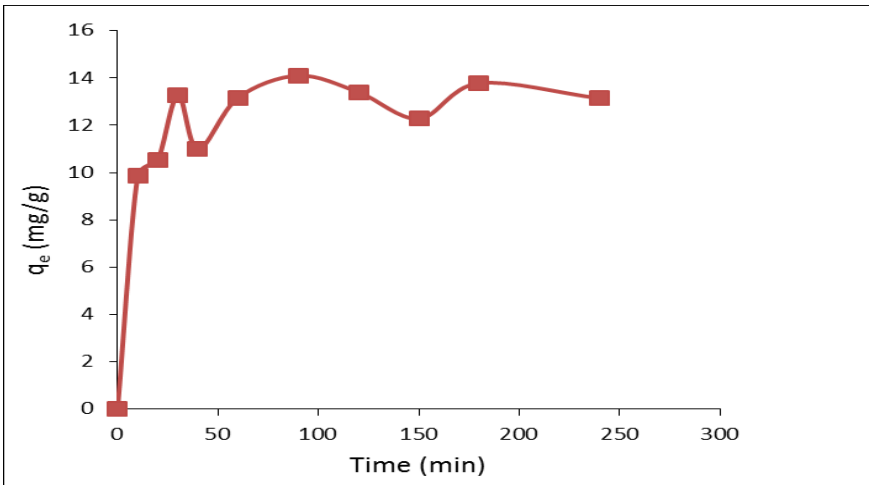
Srl. No.	MMGNs	293K	303 K	313 K
1.	**Langmuir**			
	KL (L mg-1)	0.028	0.067	0.14
	qm (mg g-1)	107.37	61.42	33.00
	R_2	0.98	0.98	0.84
2.	**Freundlich**			
	1/n	0.77	0.92	0.65
	KF (L mg-1)	3.86	2.68	4.14
	R_2	0.98	0.85	0.90
3.	**Temkin**			
	K_T	13.82	12.39	10.62
	f	0.58	0.66	0.64
	R_2	0.97	0.94	0.87

Table 2 Kinetic parameters MMGNs

Srl.No.		
1.	**Pseudo second order**	
	k2 (g mg-1 min-1)	0.0223
	qe (mg g-1)	15.45
	R2	0.9856
2.	**Intraparticle diffusion model**	
	ki (mg g-1 min-1/2)	0.5027
	c (mg g-1)	8.36
	R2	0.9710
3.	**Bangham model**	
	A	0.2413
	K_0	0.0068
	R_2	0.9759

Table 3 Thermodynamic parameters M-GNPs

Srl.No.		293 K	303 K	313 K
1.	ΔG (kJ mol-1)	-1.66	-1.30	-1.14
2.	ΔH (kJ mol-1)	-9.34		
3.	ΔS (J mol-1)	-26.31		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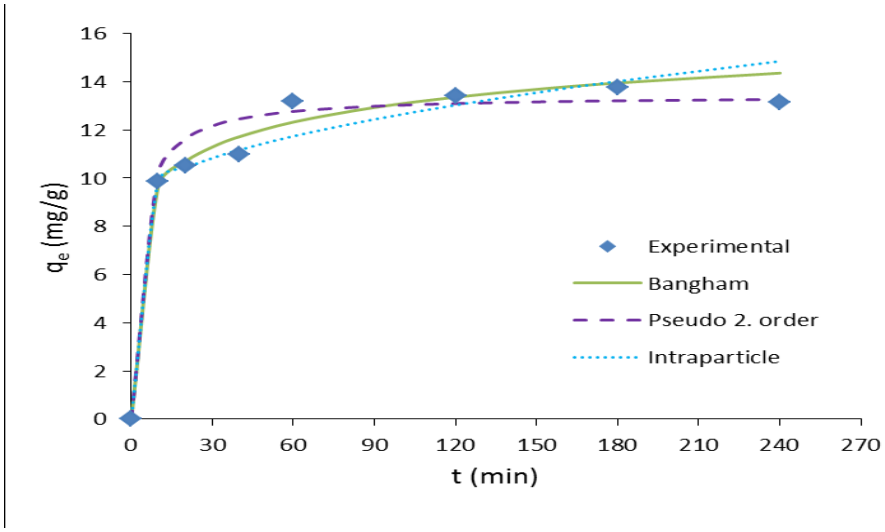
14
12
10
8
6
4
2
0
q_e (mg/g)
0
50
100
150
200
250
300
Time (min)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14
12
10
8
6
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q_e (mg/g)
0
30
60
90
120
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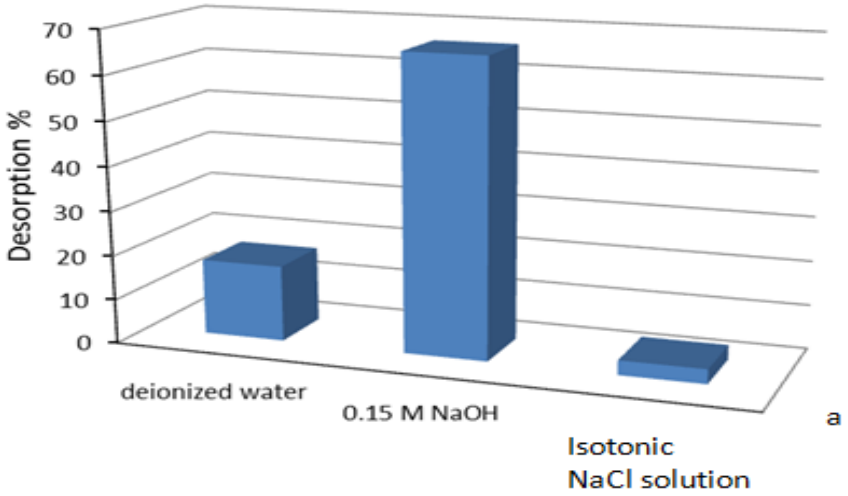
210
240
270
t (min)
Experimental
Bangham
Pseudo 2. order
Intraparticle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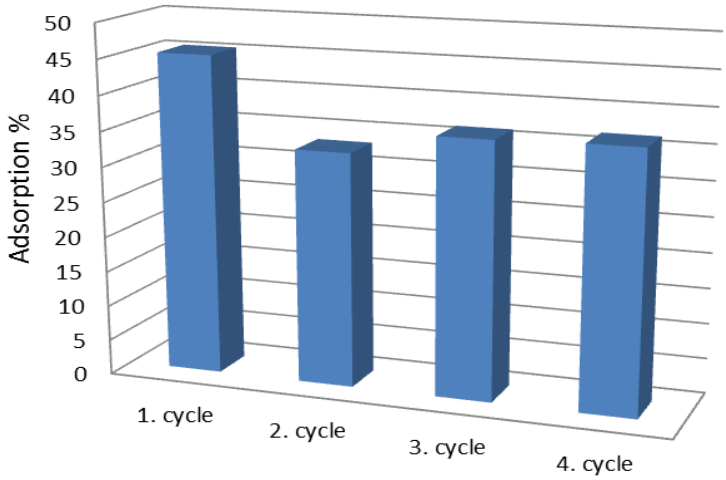
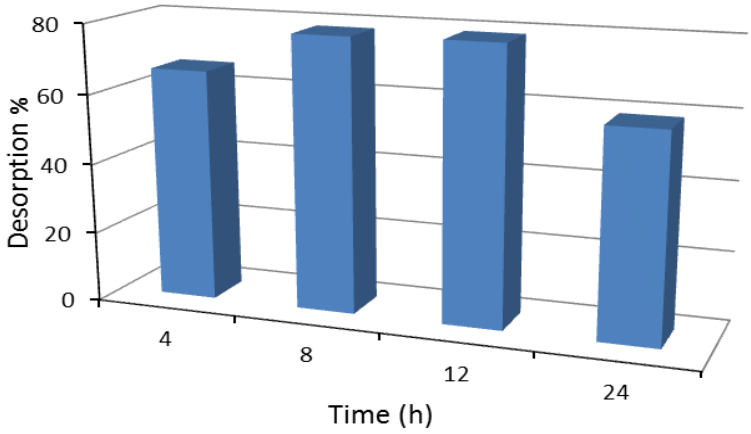
50
40
30
20
10
0
Desorption %
deionized water
0.15 M NaOH
Isotonic
NaCl solution
a





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