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Removals of Some Sulfonamide Antibiotics from Surface Water Using Fe3O4/GO Nanocomposite

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Abstract

In tis study, in order to remove the sulfonamide antibiotics namely Cotrimoxazole, Erythromycin and Sulfatrim Fe3O4/GO nanocomposite was generated under laboratory conditions. The important operating parameters (pH, antibiotic döşe nanocomposite dose, and contact time) affecting the adsorption system were examined. As a result of the conducted experiments, it was determined that the optimal operational conditions for maximum antibiotic removals was 1, 2 mgL Fe3O4/GO, 100 mg/l Cotrimoxazole, Erythromycin and Sulfatril concentration at pH= 8.00 after 40 min. contact time. SEM, XRD, TEM and XPS analyses were performed to reveal the morphological and functional properties of Fe3O4/GO. Among the applied pseudo second order and first order kinetics it was found that the sulfonamide antibiotics were adsorbed to Fe3O4/GO nanocomposite according to Pseudo second order kinetic with R2 of 0.99 and k2 values of 12.96 × 10−1, 10.46 × 10−1 and 8, 77 × 10−1 g/(mg·min) for Cotrimoxazole, Erythromycin and Sulfatrim, and with adsorption yields of qe of 156 mg/g, 128 mg/g, and 105 mg/g,respectively.

Keywords: sulfonamide; antibiotic; cotrimoxazole; erythromycin; sulfatrim; fe3o4/go; adsorption; pseudo second order

Introduction

Sulfonamides or sulfa drugs are a class of antibiotics that target bacteria causing infections. These classes of drugs are generally broad-spectrum antibiotics that act on a wide range of bacterial types and are therefore employed in treating many kinds of bacterial infections (1,2). Sulphonamides do not kill bacteria, but it interferes with the ability of bacteria to grow and multiply Sulfonamides are mainly used to treat bacterial infections and some fungal infections (3,4). As they tend to concentrate more in the urine, they are most effective against urinary tract infections. Sulfonamides, a class of antibacterial drugs, have been commonly used in medical and veterinary applications to treat numerous human and animal infectious diseases (5,6). Because of the persistence and relatively high mobility of these groups of antibiotics in the environment, they can enter the groundwater and be carried into aquifers and surface waters ; therefore, the establishment of an effective method for the determination of trace sulfonamid is necessary. Graphene, as a new allotrope of carbon, has a high profile in the scientific and engineering communities (7,8). Graphene oxide (GO) is the synthetic precursor of graphene. It possesses a large surface area and exhibits fast carrier mobility and excellent optical transparency, which makes it a novel SPE adsorbent. The graphene-based SPE and MSPE methods have been used to enrich various compounds for environmental analysis, food-safety analysis and bioanalysis(10,11). Recent reports have demonstrated that graphene and graphene-based materials are outstanding SPE materials that provide high extraction efficiencies and enrichment factors, and low cost and low consumption can be attained (12). A recent study indicated that graphene and graphene-based materials exhibit higher adsorption capacities for analytes with benzene-ring structures because of π-π stacking interactions. Magnetic graphene was employed as the adsorbent for the extraction of sulfonamid antibiotics from environmental water samples to expand the applications of graphene in analytical chemistry. It was developed a Fe3O4/GO-MSPE method and used it to preconcentrate several polycyclic aromatic hydrocarbons in environmental water samples (3-9). Four pharmaceuticals (sulfamethazine, metronidazole, norfloxacin, and 4-acetaminophen) were removed effectively by Fe3O4-graphene oxide viaphotocatalysis, and adsorption. In a study, the effects of parameters such as pH of the solution (3-11), the adsorbent quantity (0.2- 4 g /L), contact time (0- 60 minutes), the initial concentration of Amoxicillin, Cephalexin, and Tetracycline antibiotics (1- 100 mg /L) and the power of lamp (6 and 18 watts) were evaluated on the removal efficiency by using Fe3O4-GO(5-7). Amoxicillin, Cephalexin, and Tetracycline removals were 87.8%, 60.5%, and 90%, respectively after 60 min at a adsorbant döşe of 4 g/l at 100 mg/l antibiotic concentrations at Ph=7. Sulfadiazine (SDZ), sulfadimidine (SDD) and sulfathiazole (STZ) were selected as target analytes to validate the extraction performance of the Fe3O4-GO nanocomposites as a adsorbent(3-7). The results indicated that the limits of detection of these sulfonamides were in the range of 0.05–0.10 μg/mL with yields aroud 80 and 85%. TC degradation demonstrated Fe3O4@GO could be resulted from the effective transfer of photo-generated electrons between Fe3O4 by GO. Moreover, the main reaction species, •OH, O2•-, 1O2 and h+, were verified by the analysis

of active species in this system. Finally, the mechanism analyses and quantitative analysis results of active species indicated that the introduction of GO accelerated the cycle between Fe(II) and Fe(III) as well as improved the effective utilization of H2O2 (the efficiency of conversion of H2O2 to •OH.

Because of the advantages of magnetic materials and the adsorption capacity of GO, we synthesized Fe3O4-GO under laboratory conditions and used it as an adsorbent to remove the Cotrimoxazole, Erythromycin and Sulfatrim antibiotic concentrations from the surface waters and research their removals by adsorption. With XRD, SEM and TEM analysis the physicochemical properties of the Fe3O4-GO nanocomposite was researched. The effects of increasing Fe3O4/GO concentration (from 0,5 to 1.0 and 1.2 mg/l and 4.0 mg/l) , pH (from 3.0 to 6.8, and 10) and antibiotic doses (1-100 mG/l) on the yields of antibiotic removals were analysed.

Materials and Methods

Preparation of Fe3O4-GO nanocomposite

To produce Fe3O4 nanoparticles (NPs), 2 g of FeCl2·4H2O and 1,6 g FeCl3·6H2O were dissolved in deionized water. 1.3 mol/L NaOH solution was degassed for 19 min and then added dropwise to the above solution in nitrogen atmosphere under vigorous mechanical agitation. The solution was heated at 28◦C for 70 mins . The resulting Fe3O4 NPs were separated by an external magnetic field and then rinsed 3 times with deionized water till the solution pH was close to neutral, and then dried overnight at 50◦C. Then Fe3O4-GO nanocomposite was prepared as follows: Oleyl amine (1,2 mL) was added into an aqueous suspension of Fe3O4 NPs (100 mL, 18 g/L) at 70◦C under agitation conditions, and the reaction was allowed to proceed for 70 mins. The resulting oleic acid stabilized Fe3O4 NPs were separated magnetically, and further suspended in 200 mL ultrapure water. 18 g of GO was dissolved in this aqueous suspension by mechanical agitation in an ultrasonication device for 35 min. The mixture was transferred to a stainless steel autoclave and heated at 160◦C for 2 hr. The solid product was magnetically separated, rinsed with an ethanol solution (95%, V/V) for 5 times, and then dried overnight at 72◦C

Characterization of Fe3O4/GO nanocomposite

Powder X-ray diffraction (XRD) patterns of Fe3O4 and Fe3O4/ GO nanocomposite were analyzed on a

X-diffractometer using Cu Kα radiation (λ = 0.15409 nm). Morphology, and surface properties were determined with X-ray photoelectron spectroscopy, scanning electron Microscopy and transmission electron microscopy.

Samples

Surface water samples were taken from the front of a farm and and land using as agricultural activities and stored in a refrigerator until use.

Adsorption experiments

To determine the adsorption kinetics of sulphonamides on Fe3O4/GO,batch experiments were performed in a series of 200 ml glass reactors . To each reactor increasing amounts of Fe3O4/GO powder and increasing amounts of sulfonamid concentrations were added. The solution pH adjusted to 3, 6 and 10 for adsorption studies. The reactors were stirred at a rate of 250 r/min at 21Oc. At certain time intervals the samples were taken out and Fe3O4/GO were magnetically removed. After filtering the supernatant the residual antibiotic concentrations were calculated. After adsorption, the Fe3O4/GO nanocomposite was washed by an ethanol /water solution.

Measurements of Cotrimoxazole, Erythromycin and Sulfatrim antibiotics

The concentrations of selected sulfonamids were measured by ultra-performance liquid chromatography-tandem mass spectrometry (MA, USA) coupled with a Symmetry C18 column (150 mm × 2.1 mm, 5-μm particle size, Waters) (7). Formic acid (0.2%, V/V) and acetonitrile were used as mobile phases A and B, respectively, with a total flow rate of 0.2 mL/min at 30◦C. Cotrimoxazole, Erythromycin and Sulfatrim antibiotics were individually analyzed under an isocratic elution condition of 95:05, 88:12, and 70:30, respectively. Both mobile phases were filtered through 0.22-μm membrane and then degassed ultrasonically for 10 min before use. The mass spectrometer was operated under the positive electrospray ionization mode and the selected ion recording (SIR) mode was adopted for quantitative analysis.

Results

XRD analysis results

The XRD pattern of Fe3O4 nanoparticle exhibited exact profile with the pure standard crystal structure of magnetite (Figure 1). For the Fe3O4/GO nanocomposite, Fe3O4 peaks was detected at 2θ = 24◦. This can be defined as the properties of Fe3O4/GO. The valance of Fe +3 remeained the same after bounded with GO(data not shown).

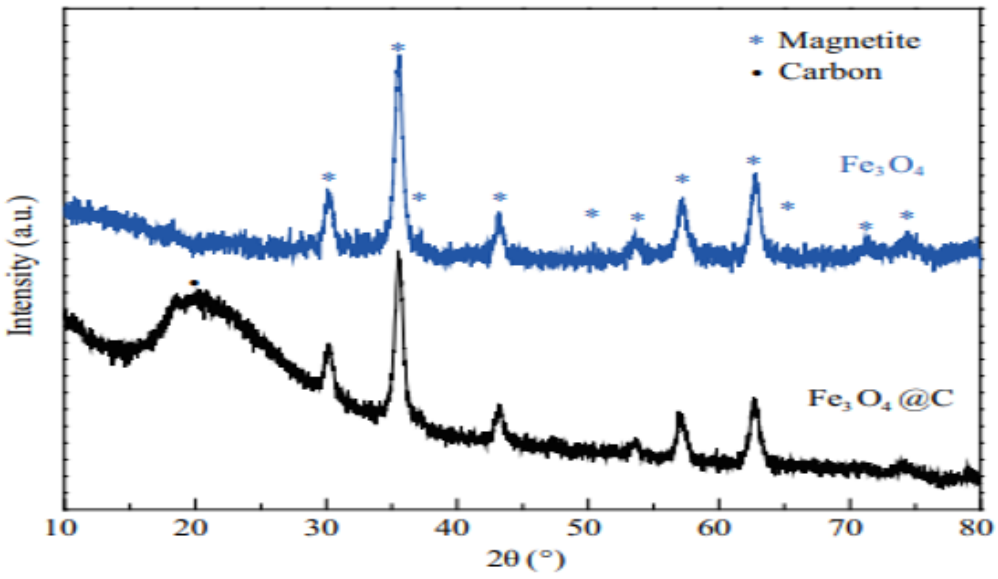

Figure 1: XRD patterns of Fe3O4 and Fe3O4/GO-C

SEM images results

The SEM image illustrated that the Fe3O4/GO nanocomposite produced under laboratory conditions exhibited an ordinary structure and the diameter of this nanocomposite is varied between 149 and 181 nm (Figure 2).

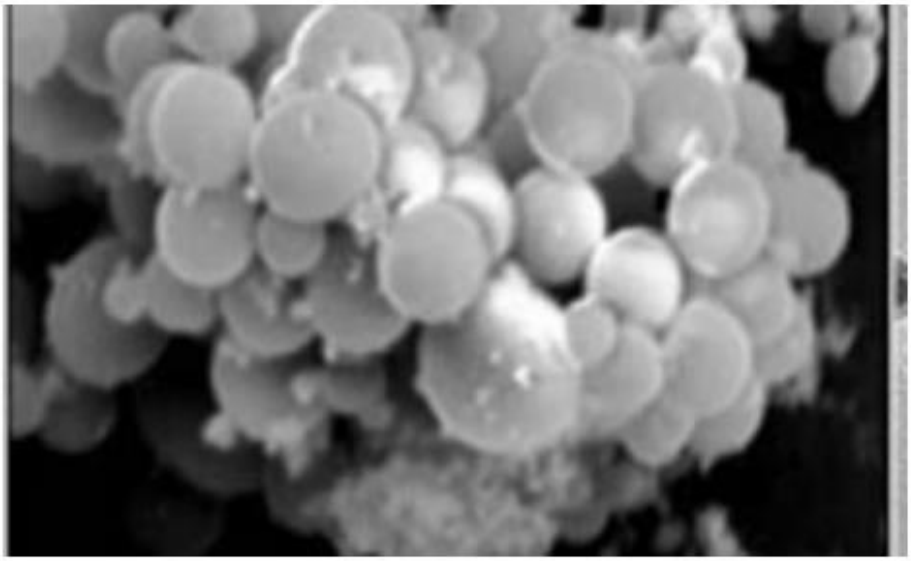

Figure 2: SEM image of Fe3O4/GO nanocomposite

TEM image

The TEM image illustrated an agglomerated colony formed by of Fe3O4 NPs and covered comletely with GO (Figure 3). The diameter of this nanoparticles was around 42 nm.

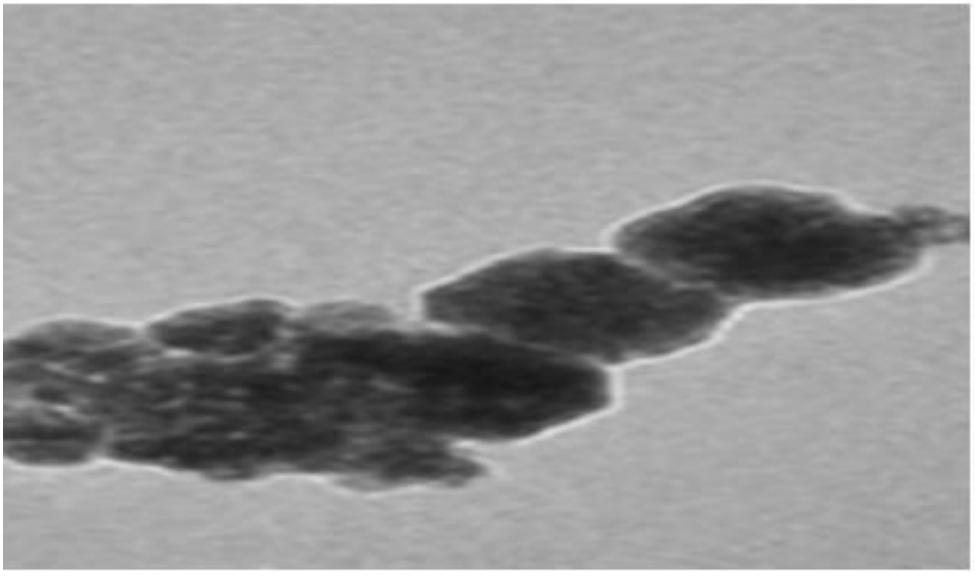

Figure 3: TEM image of Fe3O4/ GO nanoparticles

XPS analysis

The ingredients of Fe3O4/GO nanocomposite was analyzed by XPS. The peaks of Fe2p3/2 and Fe2p1/2 were found at 12.80 and 798.88 eV, respectively, in accordance with those of Fe3O4 (Figure 4). The Fe3O4 peaks was originated from pure Fe3O4.

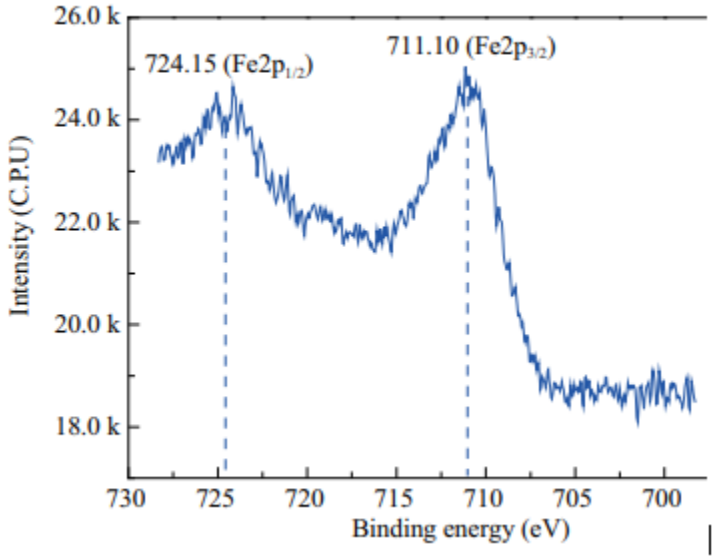

Figure 4: XPS analysis of Fe3O4/GO nanocomposite

The pH effect

The removal effciency of all sulfonamid antibiotics increased with increasing pH value from 3.0 to 6.8, and this removal fluctuated with increasing of pH values 6.9 to 8.0(Figure 5) . The removal rate of both antibiotics was maximum at pH 8.0 because electrostatic repulsive force was affected and increased at pH= 8.0. For the pH values > 8.00 a negative surface charge on the surface of Fe3O4/GO nanocomposite was occurred and this phenomenon reduced the adsorption rate. The transfer frequency of hydrogen ions of antibiotics increased when the pH was high than neutral. This results with increasing of antibiotic yields. The maximum yields were 98%, 95% and 92% for Cotrimoxazole Erythromycin and Sulfatrim antibiotics, respectively.

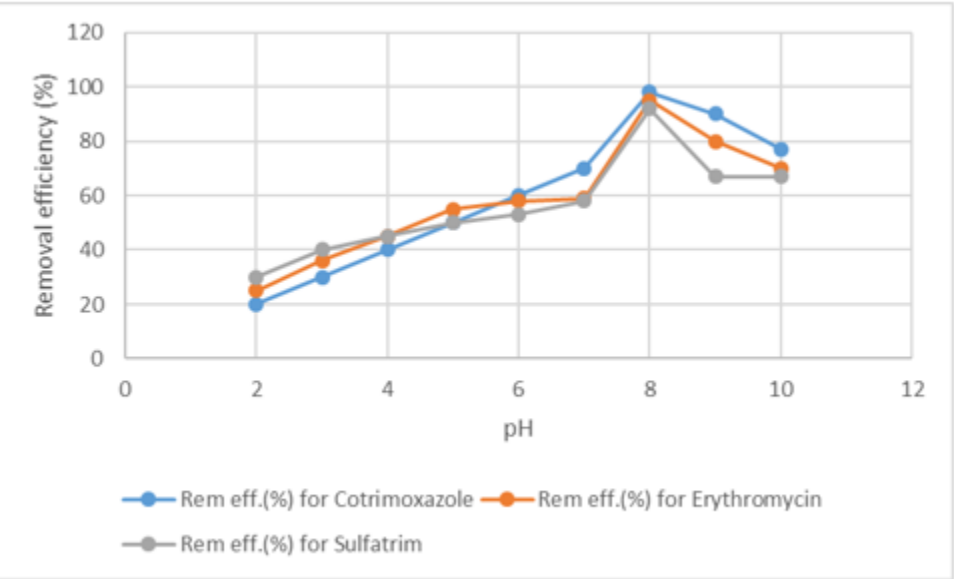

Figure 5: Effects of Ph on the removals of sulfonamid antibiotics

Effect of nanocomposite dose

Figure 6 shows the effect of Fe3O4/GO nanocomposite concentration on the removals of Cotrimoxazole Erythromycin and Sulfatrim antibiotics. As the Fe3O4/GO concentration was increased from 0,5 to 1.0 and 1.2 mg/l at pH= 8.0 at a room temperature the removal yields of Cotrimoxazole Erythromycin and Sulfatrim antibiotics was notably fluctuated from 55%, 45% and 40% to 99%, 97% and 95%, respectively(Figure 6). The number of adsorption and binding sites increases with nanocomposite dosage for the increase in removal efficiency. With an increase in nanocomposite dose from 1.2 to 4.0 mg/l, the removal efficienciens of all antibiotics firstly declined sligtly, then reached a plateau and remained the same. The reason is that a lower nanocomposite dose has relatively more existing reaction and binding sites in the surface area.

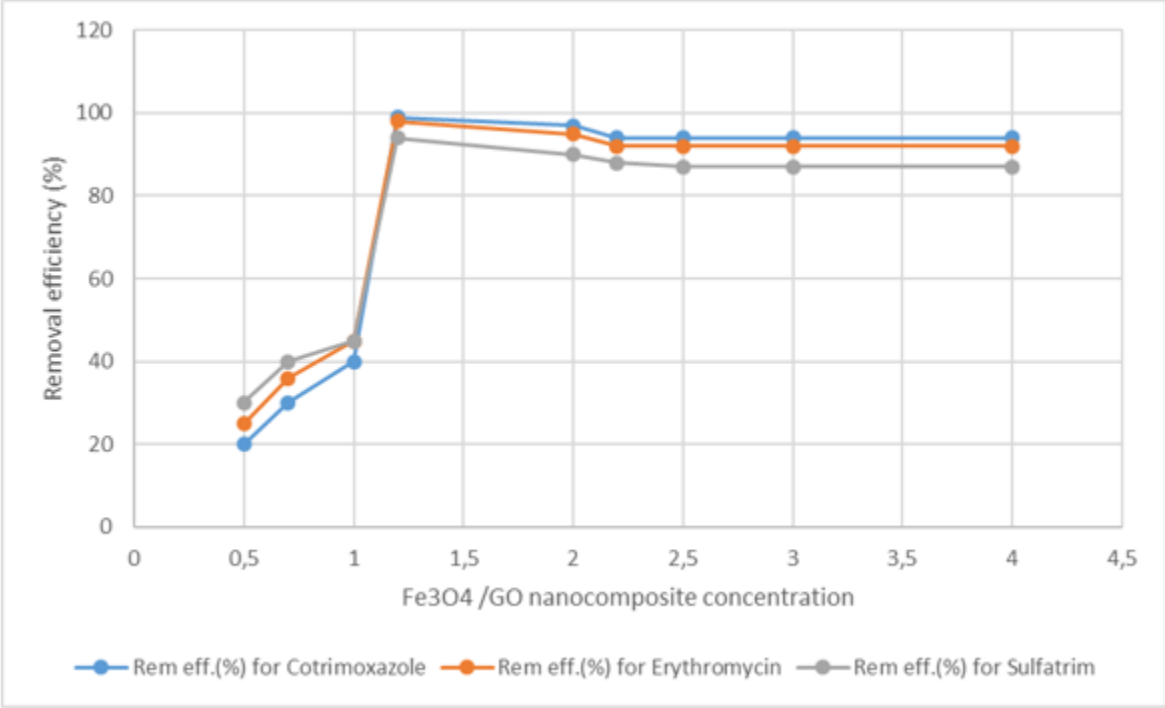

Figure 6: Effects of Fe3O4/GO nanocomposite concentrations on the removals of Cotrimoxazole Erythromycin and Sulfatrim antibiotics

Effects of Cotrimoxazole Erythromycin and Sulfatrim antibiotic concentrations

The Cotrimoxazole Erythromycin and Sulfatrim antibiotic concentrations were increased from 1 mg/l up to 100 mg/l to detect the maximum removals with adsorption process. In order to simulate the surface water the antibiotic concentrations were not elevated. At all antibiotic concentrations 99%, 97% and 95% Cotrimoxazole Erythromycin and Sulfatrim yields was detected for optimized conditions (Figure7).

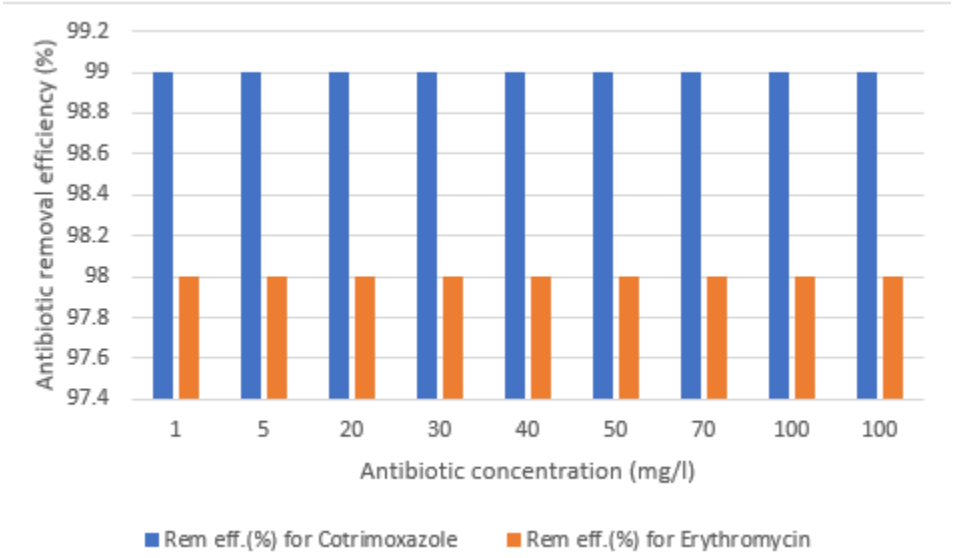

Figure 7: Effects of antibiotic concentrations on their yields at a Fe3O4/GO concentration of 1.2 mg/l at 21 Oc

Adsorption kinetics

The adsorption of Cotrimoxazole Erythromycin and Sulfatrim antibiotics on the surface of Fe3O4/GO was fast in the 40 min and remained same afterwards(Figure 8). The adsorption equilibrium was reached at 40 min, when the removal efficiencies of the Cotrimoxazole Erythromycin and Sulfatrim antibiotics were 98%, 87% and 85%, respectively. The adsorption at short times can be defined by the presence of active points on the surface of Fe3O4/GO nanocomposite. These active points on the surface of Fe3O4/GO were occupied by the antibiotics wetheen 40 mins and then adsorption process cessed.

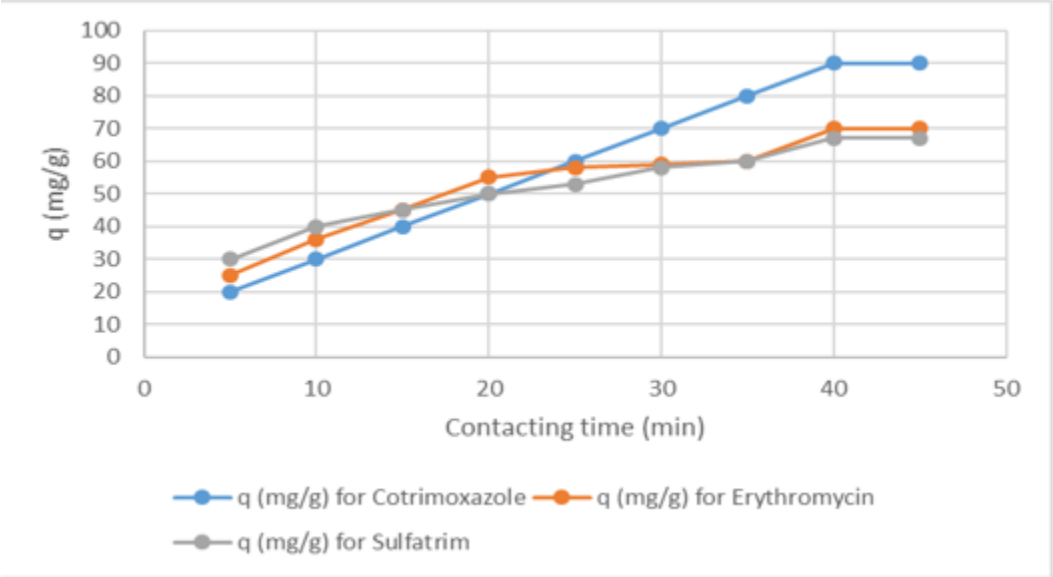

Figure 8: Adsorption kinetics of Cotrimoxazole Erythromycin and Sulfatrim antibiotics on the surface of at a Fe3O4/GO concentration of 1.2 mg/l at 21 Oc

Determination of Adsorption kinetic constants

The kinetic data of antibiotics adsorption on Fe3O4/GO was applied to pseudo second order and pseudo first-order kinetic modesl to determine the suitable kinetic constants in the removal of Cotrimoxazole Erythromycin and Sulfatrim antibiotics.

Pseudo second order reaction kinetic can be expressed with Equation 1

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

(Eq.1)

Pseudo first-order kinetic model by Lagergren can be expressed with Equation 2.

ln (qe-qt)=lnqe-k1.t **(**Eq.2)

Where, k1 and k2 (g/(mg·min)) is the adsorption rate constants in pseudo second and first order kinetics ; qt (mg/g) and qe (mg/g) exhibited the adsorbed concentrations of antibiotics to Fe3O4/GO nanocomposite at time t (min) under steady-state conditions . The adsorption kinetic parameters were obtained through model simulation and was summarized in Table 1. The adsorption rate constants (k2) of Cotrimoxazole, Erythromycin and Sulfatrim antibiotics were 12.96 × 10−1, 10.46 × 10−1 and 8, 77 × 10−1 g/(mg·min), and the adsorbed antibiotic doses (qe) were 156 mg/g, 128 mg/g, and 105 mg/g . The pseudo first order kinetic data exhibited low kinetic constans for Cotrimoxazole Ery8thromycin and Sulfatrim antibiotics. In this kinetic the adsorption rate konstants (k1) for Cotrimoxazole, Erythromycin and Sulfatrim antibiotics were 2.23 × 10−2, 1,86 × 10−2 and 0,99 × 10−2 g/(mg·min), and the adsorbed antibiotic doses (qe) were 23 mg/g, 12 mg/g, and 8 mg/g. There it can be conluded that all sulfonamid antibiotics used in this study were adsorbed and removed according to pseudo second order reaction kinetic.

Table 1. Adsorption kinetic model of Cotrimoxazole, Erythromycin and Sulfatrim antibiotics with R values

Kinetic type	Antibiotics			R values
	Cotrimoxazole	Erythromycin	Sulfatrim	
Pseudo second order kinetic model				
qe(mg/g)	156	128	105	99
k2 g/(mg·min)	12.96 × 10−1,	10.46 × 10−1	8, 77 × 10−1	99
Pseudo first-order kinetic model				
qe	23	12	8	71
K1 g/(mg·min)	2.23 × 10−2	1,86 × 10−2	0,99 × 10−2	69

Conclusions

In this investigation, magnetized Graphene Oxide nanoparticle was used as an adsorbent for Eliminating Cotrimoxazole, Erythromycin and Sulfatrim. The optimal conditions for enhancing the removal efficiency in the adsorption of antibiotics were as follows: the contact time Cotrimoxazole, Erythromycin and Sulfatrim antibiotic concentrations, Ph and Fe3O4/GO should be 40 min, 100 mg/l , 8,0 and 1,2 mg/l, respectively. As it was shown in the results, the pH adjustment was effective in the degrading of antibiotics, which can be attributed to the tendency for positive charge adsorption by antibiotics at

pH= 8.0. In basic conditions it tends to be less agglomerate than neutral whereby the specific surface area of the Fe3O4/GO nanocomposite grows.With a higher specific surface area, the amount of absorption of pollutants would raise.

According to the contact time, it can be concluded that the extent of removal has been ascending over time until reaching a specific point after a time of 40 min. With large amount of adsorbent, not significant reduction in antibiotic yields was observed. At all antibiotic concentrations used the removals were found to be high.

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