Egypt.J.Chem. **Vol. 63**, No. 6. pp. 2097 - 2110 (2020)

Egyptian Journal of Chemistry
http://ejchem.journals.ekb.eg/

Removal of Some Chemical Residues in The Effluents of Pharmaceutical Industries Using Magnetic Charcoal

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WIDESPREAD occurrence of pharmaceuticals has started to attract attention as aquatic micropollutants that might have been affecting the ecological system in trace amounts. The risks associated with their introduction into wildlife habitats is becoming an important issue for both regulators and the pharmaceutical industry, because of incomplete elimination of pharmaceuticals wastewater and their metabolites. In this study there are different classes of pharmaceuticals nonsteroidal anti inflammatory (naproxen) and psychoactive drug CNS stimulants (caffeine). This work aims to remove some of pharmaceutical residues in industrial wastewater.The identification and quantification of chemical and pharmaceutical residues was explored using Gas Chromatography with Mass detector GC/MS spectrometer and the analytical method was used Environmental Protection Agency method (EPA625) determination of the concentration in industrial wastewater using liquid chromatography-based tandem mass spectrometry LC/MS/MS spectrometer with electrospray ionization (ESI) and the analytical method was used (EPA 1694). The study recorded occurring of different types of pharmaceutical residues with different concentration levels in wastewater. The concentration levels in wastewater were detected for caffeine at 9465 ng mL^{-1} and for Naproxen at 2 ng mL^{-1} these concentrations representing about 500 fold higher than international safety margin of treated wastewater that the studies conducted in the United Kingdom, the USA and Australia have shown that concentrations of pharmaceuticals in water are typically less than 0.05 ng mL^{-1}. Magnetic activated carbon (MAC) is proposed as a new techniqe for the adsorption of pharmaceutical residues (Caffeine and Naproxen).The isotherms as well as adsorption kinetics are explored. The results obtained high adsorption capacity of caffeine and naproxen over MAC which has reached 1.8 mg g^{-1} and 1.6 mg g^{-1} after 15 min for both caffeine and naproxen. First order model is fitted well with the experimental results through a correlation coefficient (0.978) for (caffeine) and second order model is fitted well with the experimental results through a correlation coefficient (0.9887) for (Naproxen). Moreover, the adsorption of both (caffeine and naproxen) on MAC is proceeded using freundlish isotherm model considering correlation coefficient (0.953 and 0.948) respectively. The benefits of using MAC are the low cost of synthesis and its easy and fast separation from solution by using a magnet.

Keywords: Magnetic charcoal, Activated carbon, Chemical residues, Pharmaceutical residues, Adsorption isotherm, Thermodynamic, Reaction kinetic.

Introduction

Water comprises four-fifths of the human body and is one of the most fundamental factors involved in many vital human interactions and studies have shown that humans can't live without drinking water more than three days [1].

Drugs and pharmaceuticals have been used for decades in the treatment of diseases, but the surprise was that there are few studies have been

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Received 25/9/2019; Accepted 13/11/2019
DOI: 10.21608/ejchem.2019.17329.2062

made about their environmental and health effect, even if specifications of drinking water does not include any indication of the limits of toxicity and damage to more than 7000 compound drug is described medically.

Pollution with pharmaceutical residues is one form of water pollution and recent researches have revealed that there are pharmaceutical residues in the water which threaten human health as a result of exposure to long-term low doses of pharmaceutical residues, especially since most of these materials are characterized by their resistance to degradation and last for many years to be degraded [2].

Over the last few decades, the occurrence of micro-pollutants in the aquatic environment has become a worldwide issue of increasing environmental concern. Micropollutants, also termed as emerging contaminants or emerging environmental pollutants, consist of a vast and expanding array of anthropogenic as well as natural substances. These include pharmaceuticals, personal care products, steroid hormones, industrial chemicals, pesticides and many other emerging compounds. They are commonly present in waters at trace concentrations, ranging from a few ng L^{-1} to several μg L^{-1}. The 'low concentration' and diversity of micropollutants not only complicate the associated detection and analysis procedures but also create challenges for water and wastewater treatment processes [3].

Among emerging pollutants, a particular attention focuses on pharmaceuticals and hormones because they may exert their activity at the very low ng L^{-1} range [4]. Most of the literature published has been on the treatment of municipal wastewater. However, there is a growing body of research that looks at the presence of active pharmaceutical ingredients in industrial wastewater [5]**.**

As pharmaceuticals were consumed in high quantities worldwide, in the range of tons per year per one pharmaceutical compound depending on the size of a country. The expectations are that these amounts will only keep increasing because of an improving health care system, discoveries of new drugs and longer life expectations of people [6]. They enter the environment from a myriad of scattered points such as Excretion through human or animal secretions or disposition of domestic drugs and pharmaceuticals and personal hygiene products in fountains sanitation or with normal household waste, ends up in wastewater purification plants, which are usually not designed to deal with these new contaminants so pouring most of these residues to water systems without treatment which pose a great threat to humans, The main sources of contamination include pharmaceutical production plants or manufacture**.** Certain pharmaceutical production facilities in pharmaceutical industries were found to be sources of much higher environmental concentrations than those caused by the usage of drugs [7]. It has been estimated that up to half of the pharmaceutical wastewater produced worldwide is released without any treatment [8], these pollutants are non-biodegradable. Studies reveled that even small amounts (ng L^{-1}) of some pharmaceuticals adverse effects on aquatic communities include endocrine disturbance as the feminization of male fish [9], development of pathogen resistance or development of antibiotic resistant bacteria [10]. In the case of the toxic impacts on human health, the degenerative and inflammatory reactions have been found in the liver of humans when exposing to diclofenac. (a type of analgesic/anti-inflammatory pharmaceutical) [11], the proliferation inhibition effects were observed for the growth of human embryonic cells under the injection of a pharmaceutical mixture (consisting of atenolol, carbamazepine, ciprofloxacin, furosemide, ibuprofen, sulfamethoxazole, etc.) [12] In addition, in laboratory studies at the University of Georgia has shown that Exposure to some pressure-lowering drugs such as (Prozac) can cause problems such as infertility and genetic mutations [13].

Since little is known about the potential chronic hazards associated with long term ingestion of pharmaceutical compounds through drinking water, So it was necessary to determine and remove these residues in industrial wastewater, where the presence of these residues in industrial wastewater may affects all the components of the environment which makes it's discharge on drainage systems harmful to health, because those compounds will enter in the water cycle and reach to drinking water. This study aims firstly to monitor some chemical and pharmaceutical residues in industrial wastewater using GC-MS and the analytical method was used (EPA625), Secondly to determine the concentration of those chemical and pharmaceutical residues in industrial wastewater using liquid chromatography-based tandem mass spectrometry LC/MS/MS spectrometer with electrospray ionization (ESI) and the analytical method was used (EPA 1694) [14], Thirdly treatment of wastewater by magnetic

activated carbon as a method for adsorption treatment.

Materials and Methods

Materials

1- Pharmaceutical standards were supplied by The El-Nile Co. for Pharmaceutical and Chemical Industries (El-Nile) Cairo- Egypt. Methanol 99.9% purity, sodium hydroxide, acetonitrile (ACN) and formic acid from Sigma Aldrich. HCl 37% purity and NH_4OH 25% from Fisher $FeCl_3$ and $FeCl_2$ from Panreac. Ultra-pure water was used thought the work (MQ) (MilliQ system; Millipore, USA.

2- Water samples were collected from the wastewater of a pharmaceutical and chemical industries facility in pre-rinsed amber glass bottles.

3- Granulated activated carbon from Chemviron-grade 207EA 12.5*40 US.

Methods

Preparation of Magnetite Using a Homogenous Method

The solutions containing 2.72 g of $FeCl_3$ and 1.0 g of $FeCl_2$ were mixed at a certain molar ratio. Then 20 mL of NH_4OH 25% was slowly injected into the mixture of $FeCl_3$ and $FeCl_2$ under vigorous stirring at temperature 60-70 ^{0}C. Before the reaction, N_2 gas was injected through the reaction medium to prevent possible oxidation. After precipitation, the Fe_3O_4 particles were repeatedly washed and filtered before drying at room temperature. The chemical reaction of Fe_3O_4 precipitation can be described as follows

$$\mathbf{Fe^{2+} + 2fe^{3+} + 8OH^- \text{------>} \ fe_3O_4 + 4H_2O.}$$

Doping of Magnetite in Activated Carbon

A solution containing 2.0 g of magnetite and 2.0 g of commercial activated carbon was prepared in 40 ml distilled water under vigorous stirring at room temperature. After 5.0 hours the doping is complete. Filtering and washing and drying in an oven at 100 ^{0}C are carried out and result showed that slower effect if MAC so a solution containing 1.0 g of magnetite and 2.0 g of commercial activated carbon was prepared in 40 ml distilled water under vigorous stirring at room temperature. After 5.0 hours the doping is complete. Filtering and washing and drying in an oven at 100 ^{0}C instead of the previous one to increase surface area and results prove that [15].

Instrumentation

The pH meter model (Hach, Sension1) equipped with reference electrode used to adjust the solutions pH, Rotor shaker 15 position model (THERMO, SHKE2000) equipped with timer used to batch experiments. Samples collected from the effluents of a Pharmaceutical and Chemical Industries facility were determined and monitored for chemical and pharmaceutical residues by (EPA 625) using GC/MS/MS This method is applicable to the determination of extractable organics in municipal and industrial discharges which collected from field in glass container then the water sample is filtered then a measured volume of sample, approximately 1.0-L extracted with methylene chloride at a pH 2.0 using a separatory funnel. The pH is adjusted by Sulfuric acid. The organic layer (Methylene chloride) extract dried, concentrated to a volume of 1 ml using Rota vapor instrument. Then analyzed by GC (varian 3800) and mass detector (varian320-MS) in full scan.

Gas chromatography conditions

Thermal program= start by 40 °C hold for 3.5 min. then increase to 250 °C by 5.0 °C min^{-1} then increase to 280 °C by 2.0 °C min^{-1}
Inlet Temp. = 275°C
Column's specification= VF5-ms (30m-0.25mmID-0.25um)

Mass detector conditions

Ion source = Electron ionization
Filament = 70 e.v
Mass range= 50-550 amu
Manifold Temp. = 40 °C
Ion source Temp. = 200 °C
Transfer line Temp. = 250 °C.

Qualitative identification of the individuals in the extract is performed using the retention time and the relative abundance of the three characteristics masses (m/z). Quantitative analysis is performed by using LC/MS/MS water collected from the effluents of a pharmaceutical and chemical industries facility were filtered and subsequently analyzed by LC/MS/MS. Each sample which was spiked by mixture of chemical and pharmaceutical residues and MAC before analysis was magnetically filtered and vacuum filtered through a 0.45-µm glass fiber filter then extracted via solid-phase extraction

(SPE) [16] and subsequently analyzed by LC/MS/MS (Agilent's 6410 triple quadruple LC/MS/MS system with ESI). The Agilent MassHunter Workstation software (version: B.01.04) was used for system control and data acquisition.

Standards optimization

Pharmaceutical standards were optimized separately**,** and MRM transitions with optimum fragmentor voltage and collision energy was selected. Table (1)

TABLE (1) MRM method parameters selected in positive and negative ion modes

Compound	Class	Ionization	MRM transitions		Collision E
			Precursor ion	Quant ion	
Caffeine	Stimulant	Positive	195.3	138.1	20
Naproxen	NSAID	Negative	229	170	15

The total ion chromatogram (TIC) in positive and negative ion mode for standard mixture of pharmaceutical compounds (Caffeine and Naproxen) is shown in Figure (1).

Figure (1) Abundance vs. acqui. time (min)

Instrument parameters

TABLE (2) Instrument parameters

HPLC (Meng, 2008)		**MS-MS**	
LC:	Agilent 1200 LC system	MS:	G6410A QQQ
Column:	ZORBAX Eclipse XDB-C18, RRHT, (4.6 × 50 mm, 1.8 µm)	ionization mode:	ESI
Column temperature:	40 °C	Mass range:	125 to 800 amu
Mobile phase A:	0.1% Formic acid/H2O	Scan time:	300 ms
Mobile phase B:	Acetonitrile (ACN)	Capillary:	3500 V
Flow rate:	0.3 mL/min	Nebulizer P:	40 psi
Gradient:	T=0, A=100%, B=0%	Drying gas:	9 L/min
		Gas temperature:	350 °C
	T=15, A=0%, B=100%		
	T=20, A=0%, B=100%	Skimmer:35 V	
	T=21.5, A=100%, B=0%		
Injection volume**:**	**1.0 µL**		

Calibration curve consists of Five points for each pharmaceutical compound from 0.1 to 0.01µg/ml (ppm) at the following concentrations (0.1, 0.075, 0.05, 0.025, 0.01 µg/ml) was prepared using linear fit with no origin treatment. In general all compounds give linear results with excellent sensitivity, with r^2 values of 0.990.

Adsorption Batch Experiments

The batch experiments were carried out to study the optimum conditions for removal processes such as solution pH, MAC dose, initial concentration of (caffeine and naproxen), contact time, ionic strength and reaction temperature. Batch experiments were carried out at room temperature (25 °C) by adding a known amount of (MAC) to 50 ml of analytes solution into number of 100 ml conical flasks sealed with aluminum foil on a rotary shaker at 250 rpm for 25 min. The effect of pH was conducted to (MAC) by adding 0.1 g of (MAC) to 50 ml of 10 µg L^{-1} analytes solution at different pH values (from 5.0 to 9.0) which adjusted by phosphate buffer solution and 0.1 M HCl or 0.1 M NaOH. The effect of adsorbent dosage was conducted by adding desired amounts of (MAC) (0.01, 0.02, 0.05, 0.1, 0.2, 0.3, 0.5 and 1.0 g) to 50 ml of 10 µg L^{-1} analytes solution at universal pH. To investigate the effect of chemical and pharmaceutical(analytes) concentration, experiments were carried out by adding 0.1 g of MAC to 50 mL of analytes solution at concentrations (0.005, 0.01, 0.02, 0.05 , 0.1 , 0.8 , 2.0 , 4.0 , 8.0 , 16 and 24 mg L^{-1}) at universal pH. Equilibrium time was conducted by adding 0.1 g of MAC to (4.0 mg L^{-1} caffeine and naproxen solution) at different time intervals of (5, 15, 30, 45, 60, 90 and 120 min). To investigate the effect of thermodynamics the experiments were carried out at universal pH, optimal concentration and optimal adsorbent dose at equilibrium time. To investigate the effect of ionic strength, experiment carried out at different concentrations of $CaCl_2$ (0.01, 0.05, 0.1, 0.3, and 0.5 M) at optimum conditions that mentioned previously.

Monitoring of chemical and pharmaceutical residues in different water samples

Water samples were taken from the effluent of a pharmaceutical and chemical industries facility.

Result and Discussion

Monitoring of chemical and pharmaceutical residues in wastewater samples

Qualitative analysis of wastewater showed that there are many organic wastewater contaminants (OWCs) as shown in Table (3).

Quantitative analysis of selected four compounds of organic wastewater contaminants (OWCs) shown in Table (4). Thomas and foster (2005) and Terns et al. (2001) reported the presence of caffeine at concentration 150 ng mL^{-1}, 42 ng mL^{-1} respectively. Jones et al. [18] found naproxen at ng m L^{-1} levels in a large englishsewage treatment plant and in Louisiana. Influent concentrations are likely to be quite variable because they are dependent upon various factors such location, socioeconomic status, pharmaceutical cost, and other demographic data.

TABLE (3) Compounds found in qualitative analysis of four samples

Compounds found in sample 1	Compounds found in sample 2	Compounds found in sample 3	Compounds found in sample 4
1-(2,6,6-Trimethylcyclohex-1-enylmethanesulfonyl)benzene	1-(2,6,6-Trimethylcyclohex-1-enylmethanesulfonyl)benzene	1-Pyridin-4-amine, 2,3-dichloro-	1-L-(-)-Menthol
2-3-Methylpyridazine	2-3-Hexanone, 2,5-dimethyl-4-nitro-	2-Benzene, 1-(dichloromethyl)-4-methyl-	2-à-Terpieol
3-4-Chloro-3-methylbut-2-en-1-ol	3-Cyclohexanemethanol, à,à,4-trimethyl-	3-9-Thiabicyclo[3.3.1] nonane,2,6-dichloro	3-Bicyclo[2.2.1] heptane-1-carboxylic acid, 7,7-dimethyl-
4-Propane, 2-(2-isopropylidene-3-methylcyclopropyl)-, trans-	4-3-Cyclohexene-1-methanol, à,à4-trimethyl-	4-Exo-ketoborneol	4-Propanoic acid, 2-methyl-, 2,2-dimethyl-1-(2-hydroxy-1-methylethyl)propyl ester
5-Phenol, 4-methyl-	5-p-Mentha-1,4(8)-diene	5-3-Ethyl-1-heptyne-3-ol	5- Propanoic acid, 2-methyl-, 3-hydroxy-2,4,4-trimethylpentyl ester
6-Phenol, 3-methyl-	6-3,5-Heptadienal, 2-ethylidene-6-methyl-	6-Bicyclo[2.2.1]heptane-1-carboxylic acid, 7,7-dimethyl-	
7-7-Octen-2-ol, 2,6-dimethyl-	7-Exo-ketoborneol	7-Phenol, 3,5-bis(1,1-dimethylethyl)-	
8-L-(-)-Menthol	8-Benzaldehyde,4-(1-methylethyl)	8-Propanoic acid, 2-methyl-, 1-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester	
9-à-Terpieol	9-Bicyclo[2.2.1]heptane-1-carboxylic acid, 7,7-dimethyl-	9-8-Hydroxy-2,2,8-trimethyldeca-5,9-dien-3-one	
10-1H-Imidazole, 2,4,5-trimethyl-	10-7-Oxabicyclo[4.1.0]heptan-2-one, 3-methyl-6-(1-methylethyl)-	10-9-t-Butyltricyclo[4.2.1.1(2,5)] decane-9,10-diol	
11-3,5-Heptadienal, 2-ethylidene-6-methyl-	11-Propanoic acid, 2-methyl-, 2,2-dimethyl-1-(2-hydroxy-1-methylethyl)propyl ester	11-1,2-Benzenedicarboxylic acid, butyl octyl ester	
12-2-(2-Chloro-2,3,3-trifluoro-cyclobutyl)-cyclopropanecarboxylic acid	12-Ascaridole epoxide	12- Phthalic acid, butyl isohexyl ester	
13-Phenol, 4-propyl-	13-Propanoic acid, 2-methyl-, 3-hydroxy-2,4,4-trimethylpentyl ester	13-1,2-Benzenedicarboxylic acid, diisooctyl ester	
14-Bicyclo[2.2.1]heptane-1-carboxylic acid, 7,7-dimethyl-	14-4,6-Dimethyl-(1H)pyridone-2,	14-lambda.-Cyhalothrin	
15Tetracyclo[5.2.1.1(2,6).0(3,5)] undecan-10-one, 4,4-dichloro-	3-(4-benzyloxyphenylmethyleneamino		
16-Exo-ketoborneol	15-Glycine, N-(2-hydroxybenzoyl)-		
17-3'-Hydroxyquinalbarbitone	16-Tetradecane		
18-Propanoic acid, 2-methyl-, 2,2-dimethyl-1-(2-hydroxy-1-methylethyl)propyl ester	17-Dodecane, 5,8-diethyl-		
19-Propanoic acid, 2-methyl-, 3-hydroxy-2,4,4-trimethylpentyl ester	18-Diisobutyl phthalate		
20-Ethanol, 2-(octadecyloxy)-	19- Dibutyl phthalate		
21-Benzoic acid, 4-ethoxy-, ethyl ester			
22-Formamide, N,N'-[1,3-phenylenebis(methylene)]bis-			
23-Diethyl Phthalate			
24-Carbamic acid, N-[1,1-bis(trifluoromethyl)ethyl]-, 4-(1,1,3,3-tetramethylbutyl)phenyl ester			
25-3-(p-Anisoylhydrazono)-N-(2-ethylphenyl)butyramide			
26-Phenol, 2-methyl-4-(1,1,3,3-tetramethylbutyl)-			
27-Spiro-1-(cyclohex-2-ene)-2'-(5'-oxabicyclo[2.1.0]pentane), 1',4',2,6,6-pen			
28- Carbamic acid, N-[1,1-bis(trifluoromethyl)ethyl]-, 4-(1,1,3,3-tetramethylbutyl)phenyl ester			
29-Phenol, 3,5-bis(1-methylethyl)-			
30-Phenol, 2-methyl-4-(1,1,3,3-tetramethylbutyl)-			
31-Phenol, 4-(1,1,3,3-tetramethylbutyl)-			
32-Diisobutyl phthalate			

TABLE (4) Concentration in (ng mL^{-1}) of two analytes in wastewater of a pharmaceutical and chemical industries facility

Sample	Caffeine conc. (ng mL^{-1})	Naproxen conc. (ng mL^{-1})
Sample1	9465	2000
Sample2	1750	1700
Sample3	25	1500
Sample4	450	1800

As shown in table (4) the quantitative analysis of water sample in agreement with Salgado et al. [19]; Sim et al., 2011 and Yu et al., 2013) as they reported the presence of caffeine at conc. 4-19 ng mL^{-1}. In our study the effluent concentration of caffeine was 9465 ng mL^{-1} which reported 500 fold higher than recommended in worldwide that the studies conducted in the United Kingdom, the USA and Australia have shown that concentrations of pharmaceuticals in water are typically less than 0.05 ng mL^{-1}. and when naproxen exposed to sunlight it's converted into two related compounds these photodegradants are predicted to be more toxic than naproxen because they have lower polarity.

Effect of pH

The study revealed that buffers affects on the dissolution rate of these pharmaceutical and chemical residues and this results in agreement with McNamara and Amidon [20] whom found that relatively minor changes in pH or buffer (citrate, acetate and phosphate) concentration can drastically affect the dissolution of a drugs so that the study of pH will depend on universal pH.

Effect of adsorbent dose

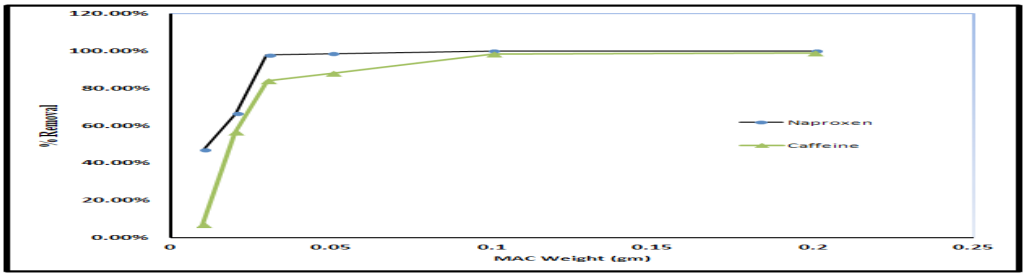


Figure (2) Effect of MAC weight on the removal % of analytes

Chemical and pharmaceutical residues removal percentage was increased by increasing the MAC dose as shown in Figure (2) By increasing the amount of MAC from 0.01 to 0.2 g, the adsorption is increased from from (7% to 99%) and from (47.5% to 100%) for, caffeine and naproxen, respectively. The reason is related to surface area or active sites great availability at higher adsorbent doses. This result agrees with Ali et al. [21] who concluded that the increase in the bio-sorption dose from 0.25 g to 0.5 g could increase the adsorption capacity of pharmaceutical from 40 mg g^{-1} to 90 mg g^{-1}. Also Hamidzadah et al. [22] reported that increasing amount of the magnetically modified activated carbon increases the contact surface area and exchangeable sites, and then increases the percent removal of analytes.

Effect of chemical and pharmaceutical residues concentration

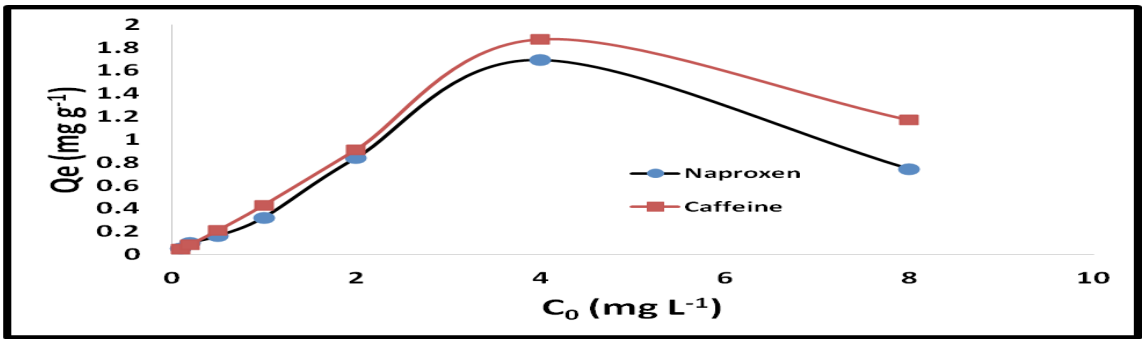


Figure (3) Effect of adsorption capacity of MAC against initial concentration of analytes

The adsorption capacity profiles of MAC with initial analytes concentration were shown in figure (3). The result displayed that the increase in the initial concentration of analytes. The adsorption capacity was also increased until to reach the maximum adsorption capacity for Naproxen, Caffeine 1.6 and 1.8 respectively at initial concentration (C_0) 4 mg g^{-1}. This is related to the high concentration of analytes which could enhance its molecules transfer from solution to MAC surface that smooth the interaction between MAC and analytes [21]. At C_0 4 mg L^{-1} the adsorption capacity decreased due to all active side was clogged by excess of analytes.

Effect of contact time

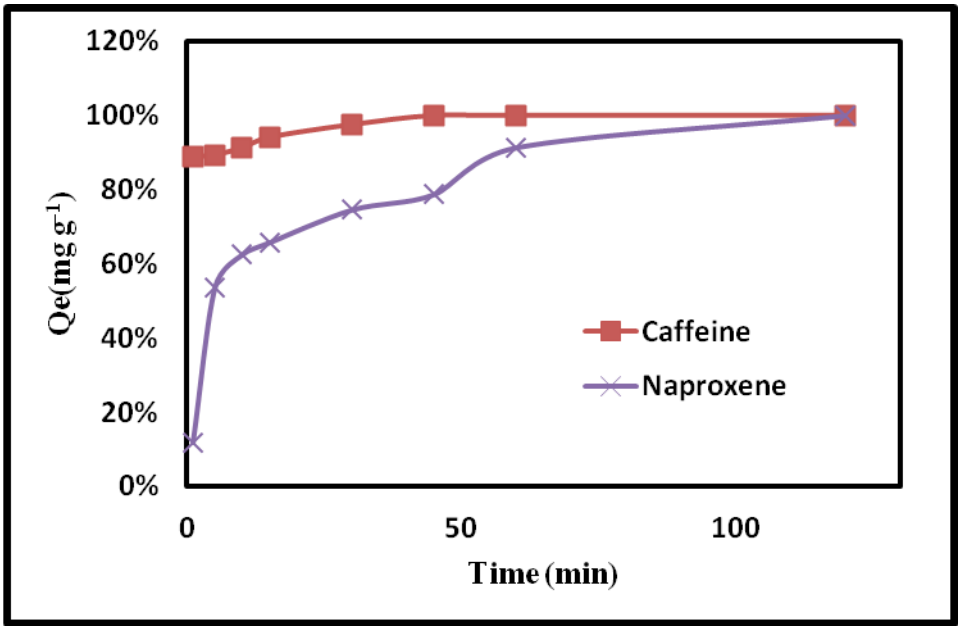


Figure (4) Effect of contact time on % removal

Figure (4) showed the percent removal of the analytes versus time for MAC. The results indicated the improvement in percent removal within time and equilibrium adsorption capacity ($q_{e\,exp.}$) was attained after 15 min for both caffeine and naproxen.This result in agreement with Çalışkan and Göktürk [23] indicating that as time increased, the adsorption capacity increased. Shikuku et al. [24] and Shikuku et al. [25] concluded that the rapid initial adsorption rate is due to availability of completely vacant active adsorption sites followed by the slow equilibrium phase attributed to saturation of the energetically favorable surfaces.

Adsorption kinetics

For realizing more data about the adsorption mechanism, different kinetic models are applied;

pseudo-first- or pseudo-second-order reaction **Eq (1, 2)**

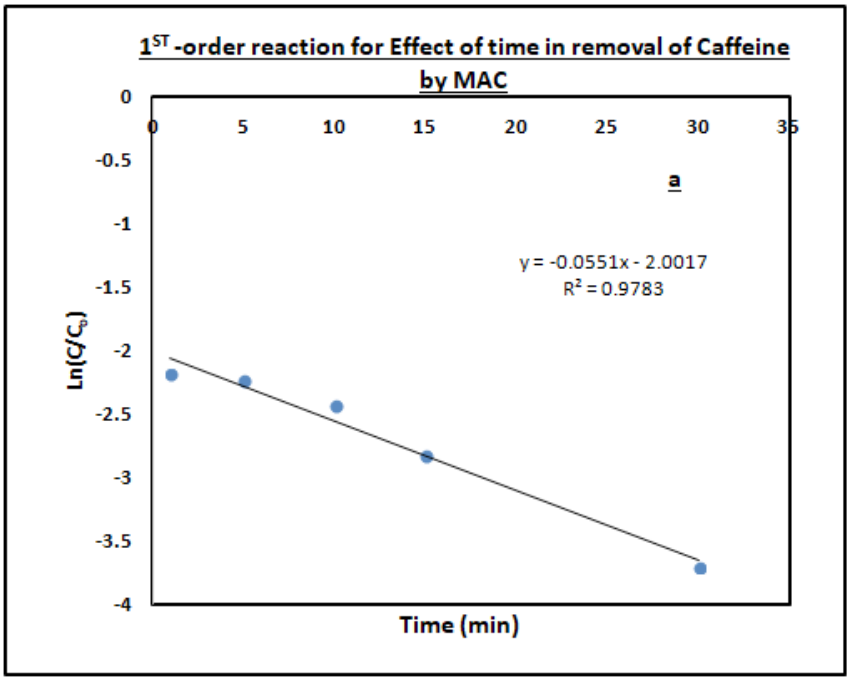
Pseudo first order:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (1)$$

Pseudo − second – order:

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

Where (t) is the adsorption time, q_e and q_t, (mg g^{-1}) are the adsorbed amount of analytes at equilibrium and time t and k_1, and k_2 are the rate constants of pseudo-first order and pseudo-second order, respectively. Adsorption kinetics of analytes describes the solute uptake rate and evidently this rate controls the residence time of the adsorbate uptake at the solid–solution interface was studied. Adsorption rate constants for the analytes was calculated by using pseudo-first-order and pseudo-second-order kinetic models which were used to describe the mechanism of the adsorption. The conformity between the experimental data and the model-predicted values was expressed by the correlation coefficients (R^2). A relatively high R^2 values indicate that the model successfully described the kinetics of analytes adsorption. Figure (5) (b) showed good compliance with the pseudo-second-order kinetic model in terms of higher correlation coefficients (0.988) for naproxen and this result in agreement with I˙lbay et al. [26] who noted that adsorption of naproxen over multi-walled carbon nanotubes and Magnetically modified activated carbon (MAC) obeyed pseudo-second-order reaction and figure (5) (a) showed good compliance with the pseudo-first-order kinetic model in terms of higher correlation coefficients (0.978) for caffeine and this results in agreement with Lakshmi and Nilanjana [27], who found that removal of caffeine from industrial wastewater obeyed pseudo-first-order kinetic model.



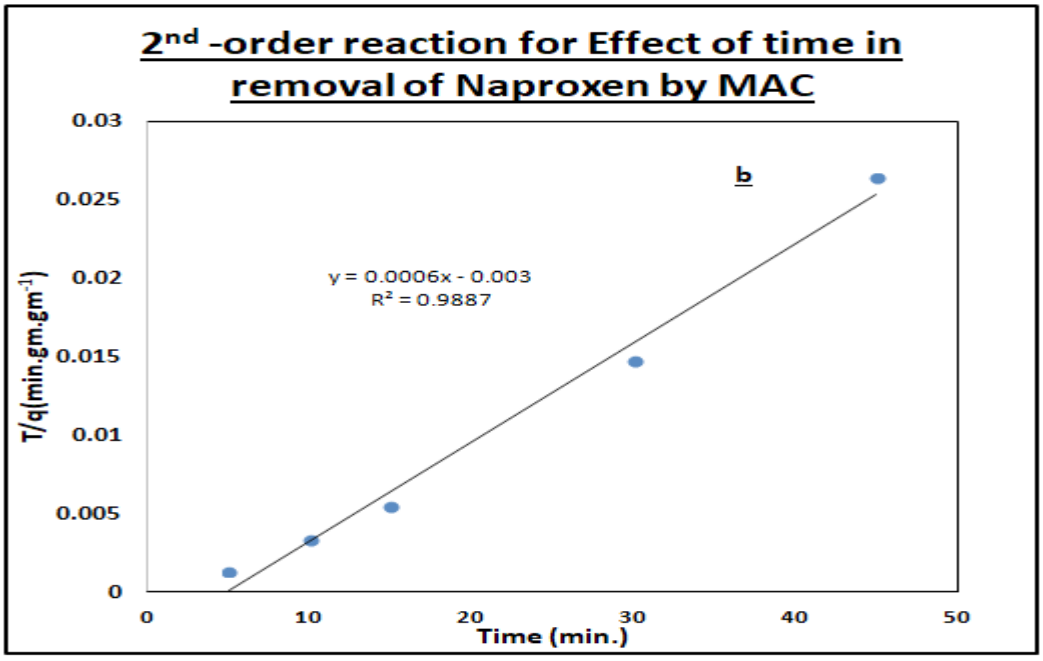


Figure (5) a and b Kinetic plots of pseudo first order for the adsorption of (a) caffeine and (b) Naproxen on MAC.

Effect of ionic strength

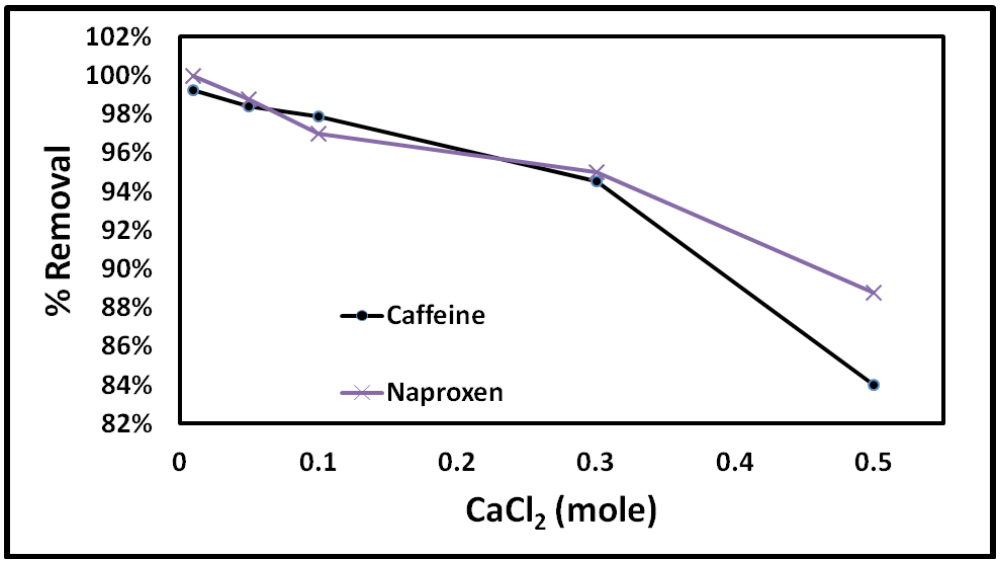


Figure (6) Effect of ions strength on MAC adsorption

The adsorption is widely affected by ionic strength as shown in figure (6) and the increase of ionic strength could lead to a decrease in the adsorption of analytes. Anirudhan and Ramachandran [28] show that ions that form outer-sphere surface complexes indicate reduction in adsorption with increasing ionic strength. Ions that form inner-sphere surface complexes show increasing adsorption with increasing ionic strength or show a little ionic strength dependence. The results worthy indicated that analytes could form an outer-sphere surface type complex on MAC. It is confirmed by by Gao et al. [29], who supposed that the increase in ionic strength would resist the electrostatic interactions. Moreover, the cation–p bonding is diminished according to the electronic screening of surface charge sites by the added Na^+.

Effect of temperature on the adsorption and thermodynamics

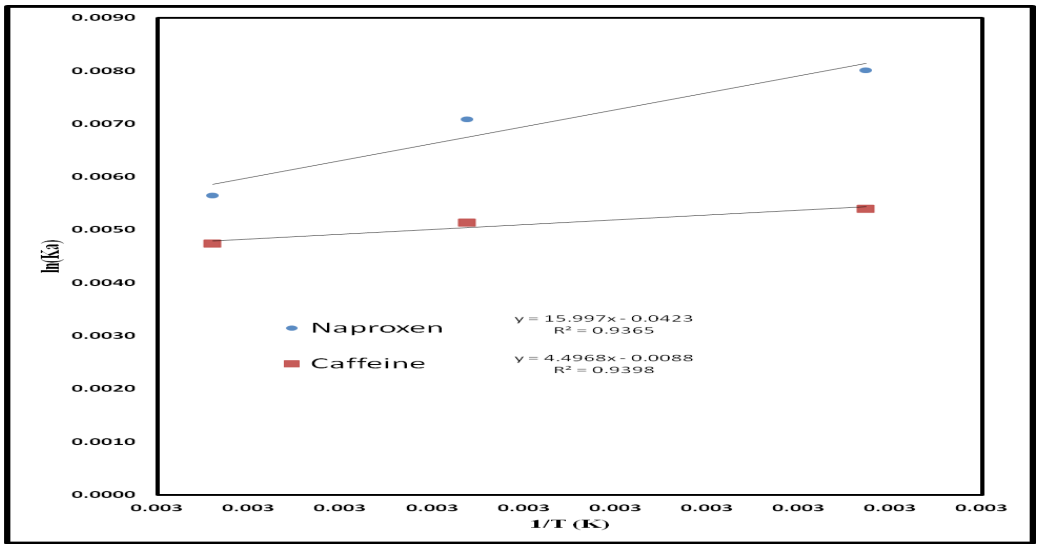


Figure (7) Van't Hoff Plots of analytes adsorption on MAC

The adsorption of analytes on MAC were carried out at different temperatures. The free energy of adsorption (ΔG°) was calculated from the following **Eq. (3)**:

$$\Delta G = - RT \ln K \qquad (3)$$

where K is the equilibrium constant and T is the solution temperature, R is gas constant (8.314 $J\ K^{-1}\ mol^{-1}$). The enthalpy (ΔH°) and entropy (ΔS°) were calculated using the Van't Hoff **Eq. (4)**.

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{R}\left(\frac{1}{T}\right) \qquad (4)$$

Values of ΔH° and ΔS° were computed from the slopes and intercepts respectively of linear variations of ln K with the reciprocal of temperature figure (7) These thermodynamic parameters are being given in Table (5)**.** As showed in in Table (5) ΔG° values were negative in the studied temperature range of 317–332 K for caffeine and naproxen. Adsorption of analytes indicated that process led to a increase in Gibbs free energy, negative ΔG° indicated that reaction is spontaneous and the negative values of ΔH° indicated that the process is exothermic. This result in agreement with Ilbay et al. [26], who concluded that adsorption of naproxen over multi-walled carbon nanotubes and Magnetically modified activated carbon (MAC) was spontaneous and exothermic. Physical adsorption and chemisorption can be classified to a certain extent, by the magnitude of the enthalpy changes, It is accepted that bonding strengths <84 K $jmol^{-1}$ are those of physical adsorption type bonds while chemisorption bond strengths in range from 84 to 420 K j mol^{-1} [23]. Based at adsorption of caffeine appears to be a physical adsorption process and adsorption of naproxen appears to be a chemisorption process. The negative values of ΔS° suggested the decreased randomness at the solid–solution interface during the adsorption of analytes in aqueous solution on MAC. The negative value of ΔS° found for adsorption of analytes in aqueous solution on MAC reveals that

a more ordered arrangement of analyte molecules is shaped on MAC adsorbent surface and this result in agreement with Ilbay et al. [26], who concluded that while naproxen adsorbed on the adsorbents, randomness was decreased on the surface.

TABLE (5) Thermodynamic parameters for analytes adsorption on MAC under different temperatures

Caffeine

T	Ka	ΔG°	Slope (ΔS°) KJ $k^{-1}mol^{-1}$	intercept(ΔH°) KJ mol^{-1}
317	**220.72**	**-14.22**		
326	**169.93**	**-13.92**		
			-0.07	-73.39
332	**113.88**	**-13.07**		

Naproxen

T	Ka	ΔG°	Slope (ΔS°) KJ $k^{-1}mol^{-1}$	intercept(ΔH°) KJ mol^{-1}
317	**2998.50**	**-21.10**		
326	**1198.50**	**-19.21**		
			-0.35	-133
332	**284.21**	**-15.59**		

Adsorption Equilibria

An adsorption isotherm is a curve show the relation between the equilibrium of an adsorbate on the surface of an adsorbent (q_e), to the concentration of the adsorbate in the liquid (C_e). (D-R) isotherm equations were used to analyze the equilibrium data in order to disclose the adsorption behavior of analytes to MAC. Linear forms of Langmuir, Freundlich, and D-R isotherm equations are given in **Eq. (5-7)**. Related constants were calculated and given in table (6)**.**

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{kq_m} \qquad (5)$$

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (6)$$

$$\ln q_e = \ln q_m - K` \varepsilon^2 P \qquad (7)$$

where q_m is the maximum adsorption at monolayer coverage in mg g^{-1}, K is the adsorption equilibrium constant related to the energy of adsorption, K_F and n are Freundlich constants representing the adsorption capacity and intensity respectively, K` is the equilibrium constant related to the adsorption energy and $\acute{\varepsilon}_p$ is the Polanyi potential it was calculated using the following **Eq. (8):**

$$\acute{\varepsilon}_p = RT \ln(1 + 1/C_e) \qquad (8)$$

where R is the gas constant (8.13 J $K^{-1}mol^{-1}$), T is temperature and E is the mean free energy of adsorption it can be calculated using the following **Eq. (9):**

$$E = (-2K)^{-0.5} \qquad (9)$$

TABLE (6) Adsorption isotherm parameters of analytes on MAC

Isotherm models	Parameter	Caffeine	Naproxen
Freundlich	R^2	**0.953**	**0.948**
Langmuir	R^2	**0.772**	**0.81**
D-R	E (kJ mol^{-1})	**4.92**	**8.03**

As seen in table (3.4), the Freundlich model gave a better fit than the Langmuir model based on correlation coefficients values (R^2) for caffeine, and naproxen. This result is in agreement with Ali et al. [21] who found that adsorption of some pharmaceuticals over biosrption obey to Freundlich model, also Zhao et al. [30] noted that caffeine adsorbance over macroporous resin obey freundlich model. In order to understand the

adsorption type, equilibrium data was tested by D-R isotherm, straight lines are obtained upon plotting (ln q_e) versus (ε^2_p) indicating that the adsorption of analytes on MAC obey the D-R isothermal equation in the entire concentration range studied q_m and K` calculated from the intercepts and slopes of the plots were given in table (3.4)**.** From the values of K it is possible to calculate the mean free energy of adsorption (E), which defined as the free energy change when 1.0 mole of ion is transferred to the surface of the solid from infinity in solution. E value is useful for estimating the type of adsorption and if this value is between 8.0 and 16 kJ mol^{-1} the adsorption type can be explained by ion exchange. The value of E found in this study is within the energy range of physical adsorption (E<8.0) [23]. As recorded in table (3.4) the calculated values of E are smaller than 8 K j mol^{-1} for caffeine and that indicating that adsorption of caffeine on MAC is physical in nature. Moreover the calculated values of E are bigger than 8 K j mol^{-1} for naproxen that indicating that adsorption of naproxen on MAC is chemical in nature and this result in agreement with Ilbay et al. [26] who concluded that the chemical adsorption occurred between the multi-walled carbon nanotubes and magnetically modified activated carbon (MAC) and naproxen.

Conclusion

From the results obtained it can be concluded that:-

- The study recorded the presence of different types of pharmaceutical residues with different concentration levels in wastewater that ends up in wastewater purification plants, which are usually not designed to deal with these new contaminants so pouring most of these residues to water systems without treatment which pose a great threat to humans.

- Even if pharmaceuticals concentrations in water were found to be much lower than the therapeutic doses, its persistence and bioaccumulation could affect our life.

- Magnetic activated carbon (MAC) considered low cost technique which can successfully minimize the concentrations of chemical and pharmaceutical residues in wastewater and its easy and fast separation from solution by using a magnet. The adsorption results of both (caffeine and naproxen)

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