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REMOVAL OF TETRACYCLINE FROM WATER BY ADSORPTION ON WATER TREATMENT RESIDUES

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Abstract

The removal of residual antibiotics from water is gaining increasing interest as they may enhance the generation of new generation of bacteria with improved resistance to such antibiotics. The available waste water treatment systems have to be supported to overcome such environmental problem because they are not capable to treat the sewage. Thus, wastewaters must be treated to remove such drugs prior to their disposal to surface water resources. Adsorption procedures are strongly introduced as promising techniques for the wastewater treatment to aid the removal of many types of pollutants including antibiotics. This work is a presenting an efficient and economic method for the removal of tetracycline, TC, at from water. The work utilizes the adsorption capacity of water treatment residue, WTR. The material was checked for the chemical composition and the adsorption activity using methylene blue. The use of WTR for Tc adsorption was studied under various conditions including sorbent content, 2-20 g/L; equilibration time 30-180 min.; and initial Tc concentration of 0.00002-0.00010 M. Experimental design was used to evaluate the optimum adsorption conditions. The effect of the operating conditions on the adsorption efficiency was established by the graphical relationships The adsorption capacity of Tc attained a value of 37.194 µmol Tet/g WTR. The sorption efficiency was inversely proportional to the initial concentration being better at low concentration (0.00002 M) and equilibrium time (within 100 mins). The optimum conditions of the adsorption are: TET Concentration, 0.00004 M; Contact time, 90 min., and WTR content of 15.5 g/L to give removal efficiency of 91.5%. The adsorption efficiency of Tc was studied in the presence of amoxicillin. Successful removal of the two antibiotics can be established within 60-90 minutes.

Key words : Water treatment residue, adsorption, antibiotic, methylene blue, tetracycline, Experimental design.

Introduction

Antibiotics exert certain load together with other pollutants on the water environment. The large and irregular consumption of antibiotics in human and veterinary medicine leads to the arrival of a large amount of antibiotics to the aquatic environment due to the incomplete metabolism and the use of conventional water treatment systems to accumulate and increase their concentrations [Danner *et al.,*(2019)]. Thus, it is an important issue to clarify disposed water from antibiotics. Ji, *et al.,* (2012)] proved that fresh water contains types of drugs like chlortetracycline, oxytetracycline, sulfamethazine, sulfathiazole, and erythromycin that have impact on two types of invertebrate organisms. They raised question: Are the current environmental concentrations safe? A great effort is directed towards the removal or at least reduction of these products in hospital wastes and develop specific plants for the filtration to minimize their impact on the water environment [Emersonde, *et al.,*(2012)]. Thus, antibiotics are recognized as emerging environment contaminants [Chen, *et al.,* (2014)] and hence they are regarded as toxic and hazardous chemicals [Wollenberger, *et al.,* (2000)]. Urban waste water treatment facilities may be hot spots for the introduction of antibiotics into our environment [Michael, *et al.,*(2013)]. Partial removal of antibiotics may be achieved by adsorption on river sediments and the process is influenced by their iron and organic contents [Barbooti, (2017)]. Hang, *et al.,* (2019)] found many antibiotics and their resistant genes in water and river sediments in china. The removal of antibiotic residues before discharging waste water in to the environment is usually costly. Case studies of providing

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cost effective solutions for antibiotic removal are urgently needed (Kim, *et al.,* (2005); Kosutic *et al.,* (2007)]. Clay minerals like bentonite, montmorillonite and kaolinite are among the mostly used adsorbents because of their high surface area and pore volume for the removal of antibiotics from water and wastewater [Barbooti, *et al.,* (2014) and Maia, *et al.,* (2017)]. The method appeared easy, efficient and cheap in comparison with filtration and sedimentation [Genc, 2015, 13]. Zhang *et al.,* 2016 [14] studied the performance of powdered activated carbon (PAC) in removing from water 6 representative groups of 28 antibiotics including namely Tetracyclines and showed that PAC exhibited high adsorption capacity for all selected antibiotics. The removal efficiency was up to 99.9% in deionized water and 99.6% in surface water at the optimum conditions with PAC dosage of 20 mg/L and contact time of 120 min. Tetracycline is among the mostly prescribed antibiotic in Iraq.[Zhang, *et al.,* (2016)] prepared and used biochar from cow manure for Tc adsorption. They proved that the adsorption was not only effect related to the physicochemical properties of biochar but also the dosage, solution pH, and ambient temperature. The adsorption on graphene oxide proved a highly effective method for the removal of Tc although it undergoes a decrease by increasing acidity (Gao, *et al.,* (2011)). A novel cu-immobilized alginate adsorbent was prepared by the sol-gel method and utilized for Tc adsorption with a capacity of 53.26/ $mg \cdot g^{-1}$. [Zhou, *et al.,* (2012)] reported an efficient removal process for tetracycline by reusable magnetic micro spheres with a high surface area. For all of the adsorbents used in their work, pH 5–6 was suitable for TC adsorption.[Yazidi *et al.,* (2020)] reported the adsorption tetracycline on activated carbon prepared from durian shell in single and binary systems. [Nie *et al.,* (2019)] investigated the effect of oxidation-induced aging on the adsorption and co-adsorption of tetracycline and Cu^{2+} onto biochar prepared from bamboo at high temperature (400 - 600 °C). Other biochar was prepared from cow manure at various pyrolysis temperatures and used for the adsorption of Tc from water. Zhang, *et al.,* (2019)] studied the adsorption of tetracycline by Cu-immobilized alginate adsorbent from water environment. The equilibrium data was fitted well with the Freundlich isotherm model and the maximum adsorption capacity for tetracycline was 53.26/ $mg \cdot g^{-1}$ at pH/ 3, 318.15/ K, and 90/ $mg \cdot L^{-1}$ tetracycline solution. The Tc could rapidly be adsorbed on *Myriophyllum aquaticum*, a floating plant, which exhibited a high potential for TC removal due to its large contact area and ion exchange, accounting for about 99% within 2/ h duration. They showed that the -OH, -COOH, and -NH2 groups are involved in the adsorption process [Guo, *et al.,* (2019)].

Recently, there was a focus on the utilization of water-treatment residuals (WTR) as a promising adsorbent for the removal of some anions [Punamiya, (2010)]. Raw water supplies from rivers is usually treated with coagulants such as aluminum and iron sulfates or ferric chloride to act on the removal of suspended and some dissolved materials and results in acceptable drinking water. The added material will combine with those removed from water and precipitate as a residual material and termed water-treatment residuals (WTR). The composition of the material varies from one place to another, depending of the type of suspended materials within the raw water and alum formulation. However, amorphous material in addition to clay, sand and some metals like Al, Fe, P, Si, Ca, and Na may be present [Makris, (2004)]. Generally, it is a heterogeneous mixture of inorganic elements. The porosity of the material porous and the presence of Al and Fe (hydroxides) improve capacity as adsorbent for many anions [Ippolitto, (2009)]. [Yang *et al.,* (2006)] sieved an Al-based WTR into several fractions and proved that smaller particles are better adsorbent for phosphate. The main effect of particle size was the improved surface area. Soil components represent the main part of WTR especially those coming from the settled sediments already suspended with water [Wagner *et al.,* (2008)]. [Leader *et al.,* (2008)], obtained almost full removal of phosphate from water within less than one hour using iron based WTR. Meanwhile, the aluminum –based WTR was effective adsorbent to remove the soluble forms of Se [Ippolito *et al.,* (2009)]. Recent reports indicated that WTR can be presented as a cheap material for the reduction of phosphate in soils, treated with animal manure [Barbooti, *et al.,* 2018, 31]. The process was fast and straight forward. Long term immobilization of phosphate proved possible with treatment by WTR.

The purpose of the present work is to evaluate the adsorption characteristics of WTR and utilize it for the removal of Tc from water.

Materials and Methods

Apparatus

The UV/Vis scanning spectra were performed on a Simadzu, Japan). The Fixed wavelength measurements were carried out on a UV/Vis 1100 spectrophotometer (EMC Lab GMBH, Germany). The shaking of the samples was done on a Genex, rotational shaker (Florida, USA). The Electron dispersive spectra were recorded on Netherlands by FEI company.

Materials and Reagents

The Tc was 98% pure material, supplied by the State Drug Industries Company, Samarra, Iraq and used without further purification.

Tetracycline chloride (Tc)

$C_{22}H_{25}ClN_2O_8$ (M.W. 480 gm/ mol, (4s,4as,5as,6s,12ar)-4-(dimethylamino)-1,6,10,11,12a-pentahydroxy-6-methyl-3,12-dioxo-4,4a, 5, 5a-tetrahydrotetracene-2-carboxamide; hydrochlorideis hydro chloride salt of tetracycline one of a broad spectrum naphthancene antibiotic.

Methylene blue was analytical reagent from Riedel de Haene, Germany. The water treatment residue WTR was obtained from a local drinking water facility during the maintenance period "Wathba". The material was dried and ground as in the procedures below.

Experimental design

The optimization was carried out by evaluating the adsorption efficiency of TC on WTR using three operation parameters: Initial Tc concentration, contact time between the WTR and the TC solution, and the adsorbent content. The experimental conditions for adsorption and the evaluation of the results were conducted using the statistical method known as Experimental design [Lawson, (2009)]. The details of the application was given by Barbooti, *et al.,* (2019)]. Five levels of each parameters were used as follows:

Initial concentration: 0.4, 0.6, 0.8, 1.0, and 1.2 x 10^{-4} M;

Contact time: 30, 52, 75, 97, and 120 min.

Adsorbent content: 2, 6.5, 11, 15.5, and 20 $g.L^{-1}$.

The program specifies the values of each parameter for the experiments (18 experiments) to be conducted. The list of run includes five experiments at the central level of each parameter to allow the estimation of the precision of the work.

Procedures

Preparation of solutions

The standard solution of MB was prepared by dissolving (0.0638g of MB in a quantity of de ionized water and complete the volume to 500 mL. The standard solution of tetracycline chloride was prepared by dissolving 0.480 g of tetracycline in a quantity of de ionized water and completion of the volume to 500 mL with water. The working standards were prepared by serial dilution with deionized water

Preparation and evaluation of WTR

The WTR sample was air-dried for 72 h at room temperature, dried at 105° C. It was then homogenized, ground and sieved to end up with 0.07 mm particle size. To decompose the organic matter (OM), a known weight of WTR was placed in porcelain dish and heated to 650°C by laboratory Furnace. The composition of WTR was evaluated before and after ignition using the EDS. The adsorption properties of WTR were evaluated by studying the removal of methylene blue (MB) from water. Four 20-ml aliquots of MB solutions of 0.0002M of MB solution were placed together with four different WTR amounts in plastic containers, capped, sealed with Parafilm and shaken for two hour at a speed of 250 rpm. The residual MB was estimated by referring to the calibration graph.

The Cation Exchange Capacity Determination

Dye cations like MB will mainly adsorb by cation exchange [Leader, J.*et al.,* (2008)]. Thus, the MB adsorption depends on the exchangeable cations of the sorbent. The CEC, was determined using the procedure used by [Ippolito, J.A (2009)] employing MB adsorption as indicator material.

Adsorption of Tc on WTR experiments

Adsorption experiments of Tc were carried out in batches:

1. The desired amounts of the WTR were placed in plastic containers (60 mL capacity) to give the desired WTR contents (2, 6.5, 11, 15.5, and 20 $g.L^{-1}$) together with the calculated volume of the antibiotic standard solution to make (0.00002-0.00004-0.00006-0.00008-0.0001 M) after dilution to 50 mL with water and the standard KCL solution (0.1 M).
2. The plastic containers were placed on the top of the rotating shaker operated at 250 rpm for the predetermined duration of time. To ensure systematic work, the containers were put in groups to be removed after the various time intervals.
3. The contents of the containers were filtered to separate the solid WTR from the solution. The filtrates were kept in glass test tubes (wrapped with dark tape) in the refrigerator until the analysis time.
4. The samples are examined with the spectrophotometer to measure the absorbance at 358 nm. The residual concentration was estimated from the calibration graph.
5. Blanc samples were prepared with all the content except the WTR, and shaken in the same way to account for any natural degradation in antibiotic solutions.

Results and Discussion

Evaluation of the WTR

The ignition of the WTR resulted in a loss of 16.56%, which is associated with the thermal decomposition of the organic matter content and the possible decomposition of some carbonates. The color of the material changed from light grey to pink. The chemical composition of the material before and after the ignition confirms such suggestion.

The results of the EDS of the WTR before and after burning are displayed in Figs. 1 and 2).

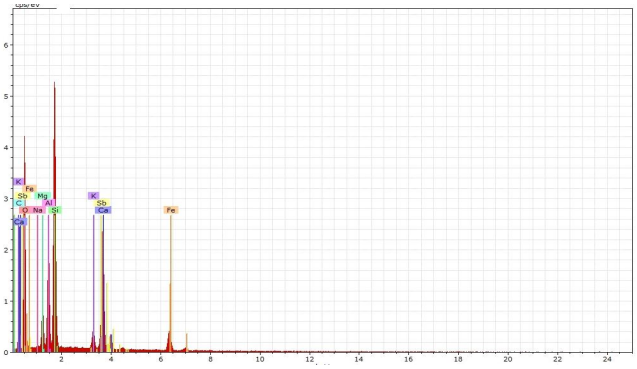

Fig. 1: The EDS spectral response of the WTR before ignition.

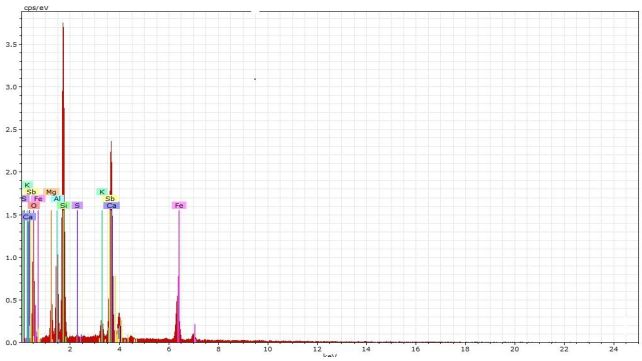

Fig. 2: The EDS spectral response of the WTR after ignition.

There was an increase in the signal of calcium accompanied by a decrease of the oxygen and complete disappearance of the carbon signal in the EDS measurement. Carbon has two sources, the calcium carbonate and the organic matter content of the WTR. The thermal treatment may contribute to the enhancement of the adsorptive power of the materials and improves the porosity as a result of inter layer spaces collations (ToorandJin, (2012)]. Chemical activation is, also, effective in increasing the activity of oxygenated aggregates and causes higher porosity of the adsorbent, thus increasing its effectiveness than thermal activation. (Maliketal., (2006) and ToorandJin, (2012)].

Adsorption characteristics of WTR by MB

The adsorption of methylene blue, MB, on materials is a well recommended method for the evaluation of the adsorption characteristics of solids (Rafatullah, *et al.,* (2010)] and Sakr *et al.,* (2015)]. Various amounts of WTR was allowed to be in contact with MB solution (0.0002 M) for 100 min. The experiments indicated complete removal of the dye by adsorption of the WTR. Fig. 3 shows the decrease of the residual concentration of the MB with the WTR content. Thus, the WTR is effective as an adsorbent to remove the dye from water solution.

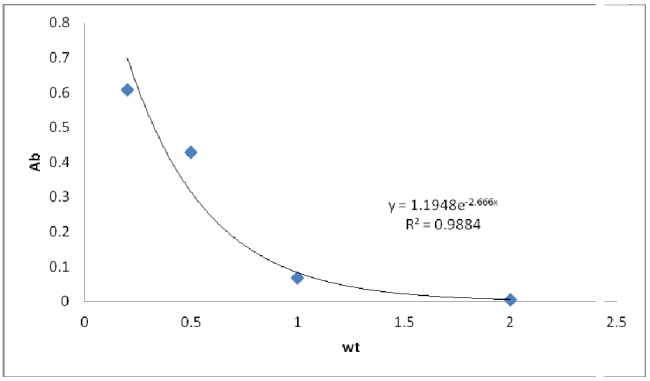

Fig. 3: Relationship between the MB (0.0002 M) spectral absorbance and WTR content after 100 minutes contact.

The CEC Determination of WTR

The cation exchange capacity, CEC, of an adsorbent is an essential property of any adsorbent. A procedure published by the Royal Society of chemistry [Taher. T, (2016)] was adopted for the determination of CEC of WTR by measuring the amount of MB adsorbed by various amounts of the sorbent and plotting the results against the corresponding WTR content (Figure 4). The slope of the curve, was used to calculate the CEC value which was found to be 20.63 µmole/g. This corresponds to 6.6 mg/g. However, smaller particle size of sorbents gave higher CEC values (Punamiya, *et al.,* (2013)].

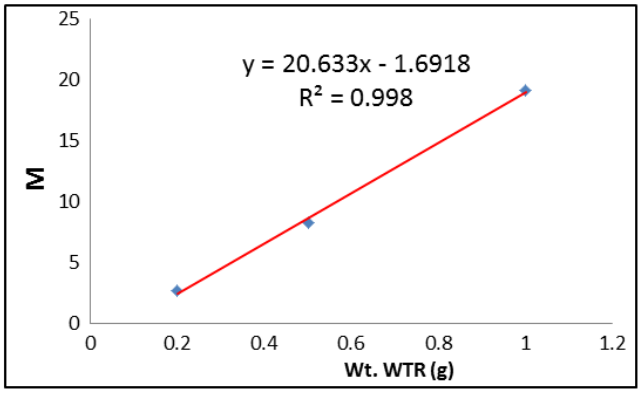

Fig. 4: Cation exchange capacity plot for the water treatment residue.

A successful adsorption is highly dependent on the surface area of the adsorbent. A mathematical relationship was reported by [Kahr, *et al.,* (1995)] between the quantity of the WTR and the amount of the adsorbed MB to estimate the surface area of adsorbents as in equation 1:

$$S\ s=m_{MB}\ /319.87_{*}\ Av\ A_{MB}\ 1/\ m_{s} \quad \ldots. (1)$$

Where

m= mass of MB at the point of complete replacement in g,

ms= mass of the WTR specimen in g,

Av=6.02 × 10^{23}/ mol (Avogadro's number)

A_{MB}=130 Å^2 the area covered by one MB molecule,

The surface area of the WTR estimated by this equation, Ss, was 6.137 $m^2.g^{-1}$.

Calibration Graphs were constructed for the determination of MB in water by plotting the absorbance values for increasing concentration of MB in water (4.0 – 60 ×10^{-6} M). The plot was linear over the used concentration range and may be described mathematically by equation 2.

$$A_{666\ nm} = 0.032\ x + 0.0037 \quad \ldots.(2)$$

Tetracycline adsorption on WTR:

The Tc concentration was measured by measuring the absorbance of the aqueous solution at 358 nm and refer the absorbance values to a calibration graph constructed between the concentration of Tc and the absorbance values. The calibration graph was linear Tc over the concentration range of 0.0002-0.0001 M. The equation (3) of the straight line calibration graph was:

$$A_{358} = 1.288x + 0.0446 \quad \ldots.(3)$$

Preliminary experiments

A set of sorption experiments was carried using a range of WTR amounts 2-20 g/L) in contact with the same aliquot of each antibiotic (0.00006 M) and shaken for 120 min. The sorption efficiency values for both materials were calculated using equation (4):

$$Eff\% = (C_0-C_i)/C_0 \quad \ldots.(4)$$

where, C_0 and C_i are the initial and residual concentration of the antibiotics. The calculated efficiency values were plotted against the corresponding sorbent content (Fig. 5). Under identical conditions and for the same amount of the sorbent, the Tc showed more than twice the sorption efficiency of AMX.

The chemical composition of Tc (Fig. 1) may account for the adsorption. Tc is characterized by many functional groups and, thus, the interaction will be high with the WTR.

The data of Fig. 4 was utilized to estimate the adsorption capacity over a range of WTR contents. The slope of the plot represents the average adsorption capacity of AMX adsorption on WTR which was μmol/ g WTR. The results are displayed in Fig 5.

Adsorption of Tetracycline

The data of adsorption efficiency was utilized to calculate the adsorption capacity of Tc over a range of WTR contents by plotting the adsorbed amount of Tc against the corresponding WTR content (Fig. 5). The slope of the plot represents the average adsorption capacity of TC adsorption on WTR which was 37.194

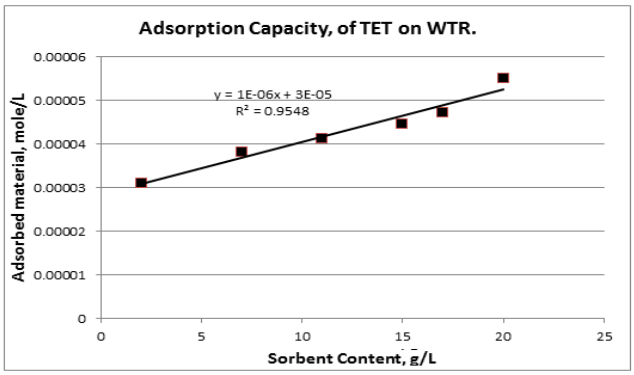

Fig. 5: Sorption capacity of Tc on the WTR.

μmol/g WTR.

Experimental design results

The data of table 1 together with their adsorption efficiency values calculated using eq. 1 were used to estimate the coefficients of the response equation (2) relating the adsorption efficiency with the experimental parameters:

$$Eff\% = a_0 + a_1 * x_1 + a_2 * x_2 + a_3 * x_3 + a_4 * x_1 * x_2 + a_5 * x_1 * x_3 + a_6 x_2 * x_3 + a_7 * X_1^2 + a_8 * x_2^2 + a_9 x_3^2 \quad \ldots.(2)$$

Where, X_1, X_2, and X_3 represent the equilibration time (min), the sorbent content (g/L) and initial Tc concentration (M). The numerical values of the coefficients table 1 represent a direct proof on the dependence of the sorption efficiency on the specific parameters. The zero value of the a_4, a_7, a_8, and a_9 reflects the negligible interaction between equilibrium time with WTR content, and the independence of the square of the parameters which indicates the linear dependence on these parameters. The negative value of (a_3) coefficient gave clear evidence that concentration has a negative

Table 1: The coefficients of the model equation.

a_0	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	a_9
2.7	1	4	-844427	0	8134	7317	0	0	0

interaction with the sorption efficiency.

Where, X_1, X_2, and X_3 represent the equilibration time (min), the sorbent content (g/L) and initial Tc concentration (M). The numerical values of the coefficients table 3 represent a direct proof on the dependence of the sorption efficiency on the specific parameters. The zero value of the a_4, a_7, a_8, and a_9 reflects the negligible interaction between equilibrium time with WTR content, and the independence of the square of the parameters which indicates the linear dependence on these parameters. The negative value of (a_3) coefficient gave clear evidence that concentration has a negative interaction with the sorption efficiency. The relatively high positive values of a5 and a6 indicated noticeable interaction of time with concentration and sorbent content with concentration on the adsorption efficiency. The adsorption efficiency was calculated for each specimen using the relation (Equation 3):

$$Eff\% = 2.7 + x_1 + 4*x_2 - 844427*x_3 + 8134*x_1*x_3 + 7317x_2*x_3 \quad \ldots(3)$$

Equation (3) was used to calculate the efficiency values for various values of each parameter at fixed values of the other two parameters. The values were plotted against variable values of the parameters and arranged to evaluate the combined effects of the three parameters on the efficiency.

Effect of initial concentration

Equation (3), above, substituted with the numerical factors was used to calculate the efficiency values as a function of various values of initial concentration at a fixed value of WTR adsorbent contents (11 g/L) at the first value of the equilibrium time to construct the first plot. The calculation was repeated for the second value of equilibrium time to have the second plot and so on. Fig. 6 shows the effect of initial tetracycline concentration on the sorption efficiency on a fixed WTR content of 6 g/L after various contact time values. The plot of the lowest equilibrium time (30 min) the efficiency was less than 10 percent. Meanwhile, the adsorption efficiency increased to 37 and 54% when using longer time of contact, namely, 52 min and 75min, respectively.

Fig. 7 shows the Effect of initial tetracycline concentration on the adsorption efficiency after 52 min of contact time with various WTR content. For the specific sorbent content the efficiency decreased linearly with the increase of the concentration. Higher sorbent content resulted in higher efficiency, because of the greater sorbent area available for the antibiotic to be adsorbed.

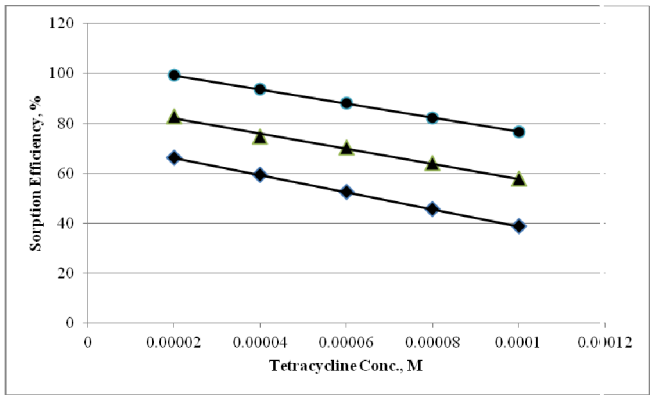

Fig. 6: The dependence of sorption efficiency of Tc on the Tc concentration after 52 min of contact time on 2 (●); 6 (▲) and 10 g/L (♦) of adsorbent content.

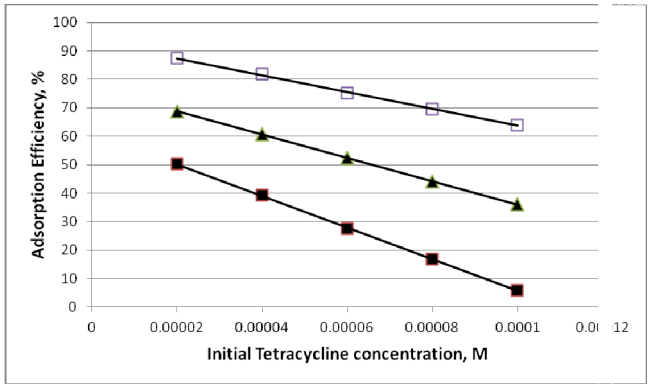

Fig. 7: The effect of initial Tc concentration on the sorption efficiency on 6 g/L WTR content after 30 min (■); 52 min(▲); and 75 min (□).

Effect of sorbent content

Equation (3), above, substituted with the numerical factors was used to calculate the efficiency values as a function of various values of WTR adsorbent contents at a fixed initial concentration of 0.00004 M at the first value of the equilibrium time to construct the first plot. The calculation was repeated for the second value of contact time of to establish the values of the second plot and so on. The dependence of the adsorption efficiency of 0.00004 M of Tc on WTR on the adsorbent content is displayed in Fig. 8 after various values of contact time. The efficiency linearly increases as the sorbent content increases. The effect of both time and concentration was complimentary, *i.e.,* a sorbent content as low as 2 g/L at after about 75 min, gave almost similar efficiency to that obtained by 10 g/L after 30 min. Generally longer contact time gave higher sorption efficiency.

Fig. 9 shows the effect of WTR content on the sorption efficiency after 75 mins for Tc various initial concentration of Tc after various equilibrium time intervals. Again the efficiency increases linearly with the sorbent

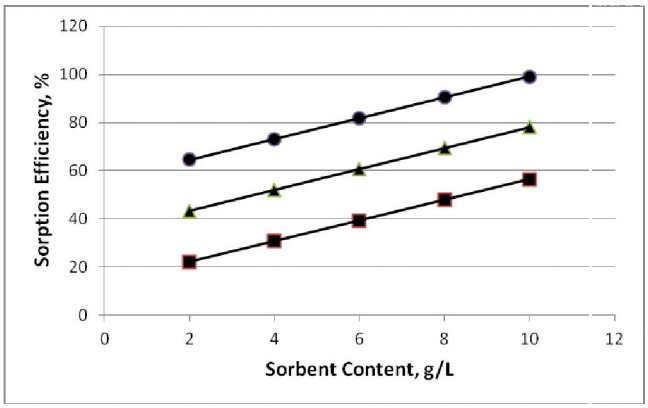

Fig. 8: The dependence of adsorption efficiency of 0.00004 M Tc on the WTR content after 30 (■); 52 (▲); and 75 minutes (●) contact time min contact time.

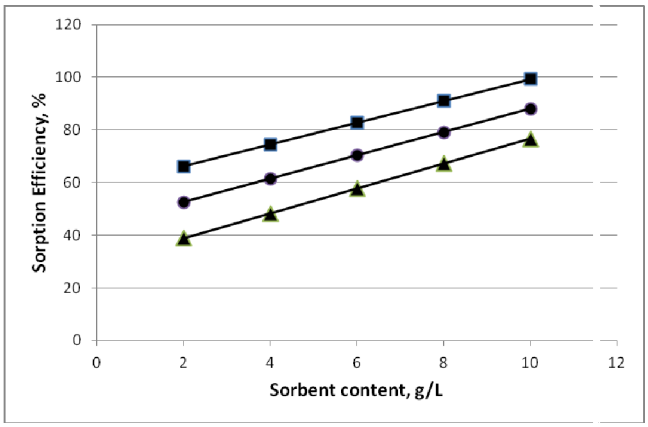

Fig. 9: Effect of WTR content on adsorption Efficiency after 75 mins for Tc initial concentration of 0.00002 M (■); 0.00006 M (●); and 0.00010 M (▲).

content for specific initial concentration. The enhancement of efficiency with the sorbent content may be enhanced by decreasing the initial concentration of the drug. At a relatively low sorbent content (2 g/L) the efficiency of adsorption of 0.00002 M, ~ 75%, resembles that of adsorbing the 0.0001 M with WTR content of 10 g/L, 73%. Thus, high sorbent content suits relatively high Tc initial concentration.

Effect of equilibrium time

Equation (3), above, substituted with the numerical factors was used to calculate the efficiency values as a function of various values of equilibrium time at a fixed value of WTR adsorbent contents at the first value of the initial concentration to construct the first plot. The calculation was repeated for the second value of initial concentration of Tc to have the second plot and so on. The dependence of adsorption efficiency of 0.00006 M on the contact time using various amounts of WTR is displayed in Fig. 10. It is clear that longer contact time resulted in higher adsorption efficiency at all the sorbent contents. About 80% of the drug was adsorbed after almost 75 min contact time with the WTR.

Figure 11 shows the effect of equilibrium time on Tc adsorption Efficiency on 6.0 g/L sorbent content for various TET initial concentrations (0.00002-0.00010 M). Adsorption efficiency increases with increasing the contact time for a fixed sorbent content and various concentrations. A contact time of about 75 min was adequate to give 100% efficiency. The values of the adsorption efficiency at the lowest concentration were the highest under similar conditions. For relatively high concentration values longer time will be necessary to achieve appreciable adsorption. At the relatively long

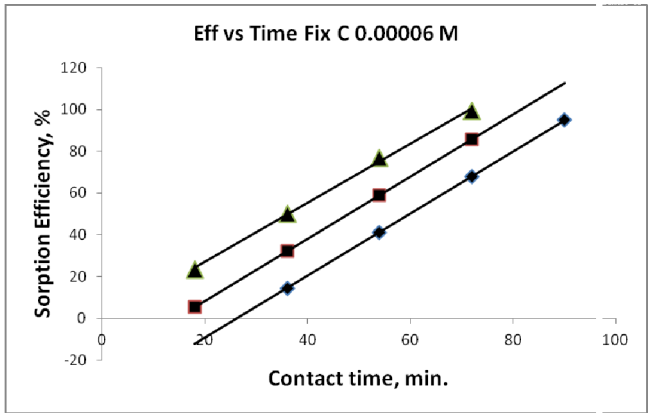

Fig. 10: Effect of equilibrium time on 0.00006 M Tc adsorption Efficiency on WTR content of 2 (♦); 6 (■), and 10 g/L (▲).

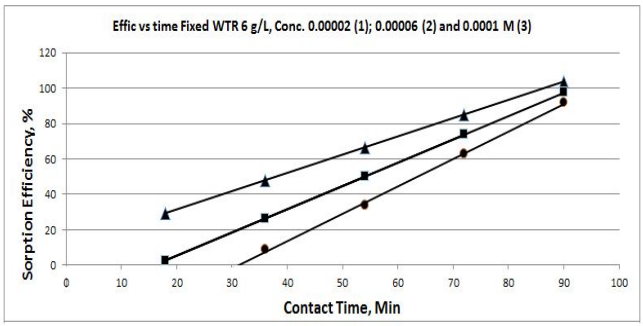

Fig. 11: Effect of equilibrium time on Tc adsorption Efficiency on 6 g/L WTR content for 0.00002 M (▲); 0.00006 M (■); and 0.00010 M (●).

contact time (75-97 min) the differences in the adsorption for the various concentration was much lower than at short contact time.

Conclusions

Water treatment residue proved successful and rather cheap sorbent for the removal of tetracycline, Tc, from wastewater. The sorption efficiency of the process is significantly affected by the initial antibiotic concentration

being better for lower the Tc concentration. The process is relatively fast and 90 minutes was found adequate for the removal of 90% of the antibiotic from water using a sorbent content of about 15 g/L.

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