Removal of Tetracycline from Aqueous Solutions using Pomegranate Peels Residues Accessing to ZRL

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Abstract

Antibiotics are harmful pharmaceuticals to ecosystems in general and aquatic systems in particular. Therefore, its remediation from water bodies is a topic of great importance for water treatment and purification workers. This research investigates the removal of one of the most famous types of antibiotics, which was tetracycline from simulated synthetic aqueous solutions by adsorption technique using non-toxic, low cost and available agricultural waste which was pomegranate peels. The adsorption experiments were performed in adsorption laboratory unit of batch mode at different operating conditions and laboratory temperature. The operating parameters studied included pH of solution, dose of adsorbent media, treatment time, agitation speed and initial concentration of tetracycline. The results showed the ability of pomegranate peels to extract tetracycline from aqueous solutions with high efficiency of 81.55%. The results also showed that the percentage of antibiotic adsorption from aqueous solutions was inversely correlated with increasing the initial concentration and acidic function of the tetracycline solution while it was directly proportional to the amount of pomegranate peels, agitation speed and treatment time. In this style, one of the most important types of antibiotics that contaminated water was disposed of by a cheap material and using a simple, economical and environmentally friendly method accessing to the principle of zero residue level (ZRL).

Keywords: *Antibiotic, Tetracycline, Adsorption, Pomegranate peels, ZRL*

Introduction

Antibiotics are defined as chemical compounds used in the treatment, prevention and diagnosis of diseases, thus preserving the physical and mental health of both humans and animals [(1)]. Today, these products pose a threat to humans and the environment as they are increasingly present in the aquatic environment, even at low concentrations of up to parts per million (ppm) as a result of increased production due to overconsumption without any treatment before disposing [(2)]. It enters wastewater with urine and excrement as well as industrial waste from pharmaceutical plants also; their environmental impact is increasing when there is a mixture of these substances with metabolites [(3)]. Recent studies have confirmed the inclusion of these formulations as contaminants, as they pose a threat to groundwater and surface water, thus causing adverse effects on wildlife and aquatic life [(4)]. These compounds include, for example, Nonsteroidal anti-inflammatory drugs (NSAIDs), antipyretics, antidepressants, diuretics, antibiotics, and anti-ulcers, whose metabolism produces new compounds that are also polluting the environment. Antibiotics come out with urine in low concentrations, and their metabolites come out with either with urine or excrement [(5)]. Conventional methods of wastewater treatment are ineffective in eliminating the contaminated effect of pharmaceutical compounds due to the resistance of some types or metabolic products to biodegradation [(6)]. Apart from traditional treatment methods, adsorption technology has recently received widespread attention as one of the candidate methods for solving the problem of water contaminated by antibiotics for its ease, efficiency and low cost [(7)]. Studies have shown that the use of adsorption technique by activated carbon is very effective in the disposal of many organic pollutants such as dyes, pesticides and aromatic compounds generally [(8)]. However, there are two problems facing this promising technique: the first problem is the high production cost of activated carbon and needed for continuous regeneration process, in addition to the part loss of this material during each regeneration process, while the second problem relates to the difficulty of sediments disposal from the surface of activated carbon or other adsorbents [9]. This led the researchers to seek for other sources to be used as adsorbents or raw materials in the preparation of activated carbon from them and also so that the amount of remaining materials are small [10]. In the last years, the concept of zero residue level (ZRL) has been applied to remedy all the problems associated with the use of adsorption technology. This concept uses the non-valuable waste as adsorption media and then utilizes from the residue adsorption process so that the amount of residual waste is close to zero [11]. The present paper aims to use the adsorption technique and the application of the principle of ZRL in the treatment of water contaminated with tetracycline, one of the common types of antibiotics through the use of pomegranate peels as a low-cost adsorbent in an economical, beneficial, low-cost and environmentally friendly method.

2. Experimental Work

Materials

2.1.1 Pomegranate peels (sorption media): The mature pomegranate peels used in this investigation were obtained from juice shops and cafes in Baghdad city as well as from domestic usage. After collection, pomegranate peels (in its originally size) were washed with excess tap water for several times before being washed with distilled water at normal temperature to get rid of any kind of impurities and dust that might be stuck to them. The washed peels were dried naturally by exposing them to the open air and sunlight for uninterrupted 48 hours and then placed in a metal bowl, immersed in fresh water and heated until boiled to remove the color and dye (tanner) from them. Finally kept in dark brown glass bottles and placed in the fridge until used.

3.1.2 Stock solutions: Real water contaminated with tetracycline (a studied antibiotic) contains many compounds and other elements that may be difficult to detect exactly or identify accurately in that type of water. Therefore, the adsorption experiments were carried out using simulated synthetic aqueous solutions (SSAS) containing tetracycline in various concentrations in order to evade nip up with any other kind of pollutants. For this purpose, an aqueous solution, called stock solution, of 1000 ppm of tetracycline, was prepared. In a volume of one liter of distilled water, 1 g of tetracycline powder packaged in capsules was dissolved to obtain the stock solution. All different concentrations SSAS of tetracycline antibiotic used in this research were prepared from dilution of the stock solution with distilled water to the desired concentration. Tetracycline concentrations were determined spectrometrically at a wavelength of λ=529 nm using a spectrophotometer according to the method described by [12]. Figure 1 shows the spectrophotometer calibration curve intended for tetracycline concentrations.

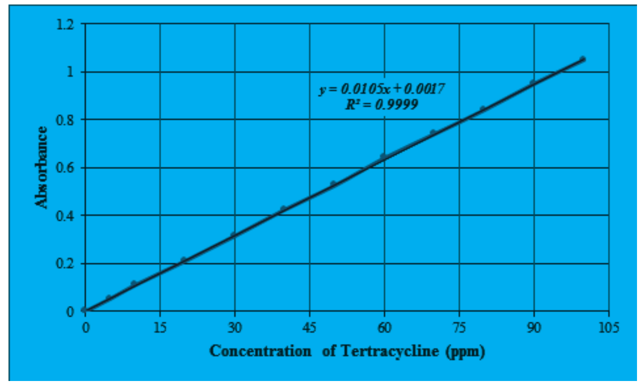

Figure 1 Spectrophotometer calibration curve of tetracycline @ wavelength of λ=529 nm

3.2 Adsorption unit: In order to identify the behavior of pomegranate peels as an adsorption media and to determine the best operational conditions that achieve the maximum tetracycline removal percentage, a concatenation of functional experiments were conducted in a laboratory adsorption unit of batch mode. In each experiment 100 ml of tetracycline solution was prepared and laboratory experiments were carried out at different operational conditions of initial concentration of tetracycline, pH of SSAS, amount of adsorbent, agitation speed and contact time. Their ranges were from (1-50) ppm and (1-8) (0.25-2.5) g of pomegranate peels, (100-400) rpm and (10-150) min. respectively and at laboratory temperature (28±2) °C. Each experiment was triplicate to increase accuracy and to reduce the experimental error. To calculate the residual tetracycline concentration at the end of the experiment, the aqueous solution was filtered using vacuum filtration to separate any residue of pomegranate peels may be present in the treated solution. A sample of the filtered aqueous solution was drawn, tested by the spectrophotometer and the concentration of the antibiotic removed was detected. The efficiency of tetracycline removal from the SSAS was determined by calculating the percentage of removal that can be found from the following mathematical relationship:

$$\%R = \frac{C_i - C_f}{C_i} \times 100$$

Where:: refers to tetracycline percentage removal, and : refer to initial and final concentration of tetracycline (ppm) respectively.

Results and Discussions

As illustrated above, the study of adsorption technology as a suggested remediation method for SSAS contaminated with tetracycline antibiotic was conducted in a batch adsorption unit. The removal process was examined at different operating conditions and using pomegranate peels as a cheap and available adsorbent. This section discusses the effect of the operational conditions used on the tetracycline removal efficiency and determination of the optimum conditions for the maximum treatment efficiency of contaminated SSAS.

3.1 Effect of Initial Concentration of Tetracycline: The results obtained from the experiments of changes the initial concentration to remove tetracycline using pomegranate peels as an adsorption media from SSAS showed that the percentage removal was increased by decreasing the value of the initial concentration and vice versa. The results also showed that the maximum percentage removal was 81.46% at the lowest initial concentration of 1 ppm while the percentage removal at the highest studied concentration which was 50 ppm was 23.19% as explained in Figure 2. Adsorption technology is great dependent on surface area and it is a constant property of adsorption media, representing the available sites on the surface of the adsorbent material at which adsorption process occurs. The number of these active sites is limited in the adsorbent and has a constant adsorption capacity for a specified number of contaminated matter particles. In the case of low concentrations of tetracycline, the pomegranate peels was able to adsorb more molecules than if the antibiotic concentration is higher; i.e., the number of non-adsorbed tetracycline molecules that will remain free in the solution will be lower at low concentrations at constant volume and therefore the efficiency of pomegranate peels as a medium of adsorption to remove tetracycline will be reduced by increasing the initial concentration of the contaminant in aqueous solutions.

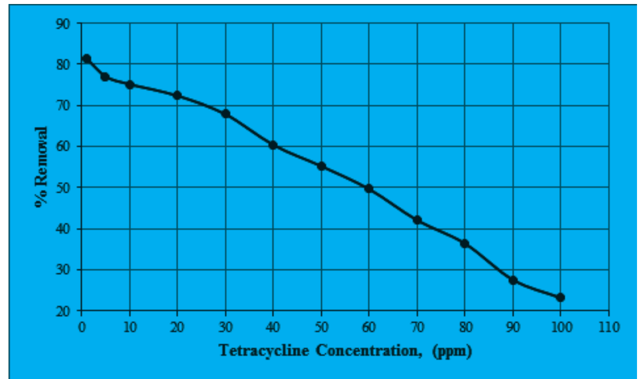

Figure 2 Effect of initial concentration on the percentage removal of tetracycline antibiotic

3.2 Effect of pH: Figure 3 shows the behavior of tetracycline adsorption process by pomegranate peels when the pH of SSAS is changed. It's obvious from above Figure that the relationship between the percentage removal and the pH of solution is inversely and the maximum percentage removal was obtained at the lowest pH value. The pH has a clear effect on the adsorption process, as it affects the charge and ionization degree of the active sites at the surface of adsorbent media. This may be due to the dependence of tetracycline ionization on the value of the pH. On the other hand, increasing the pH leads to an increase in the concentration of negative hydroxide ions (OH^-) in the solution, which generates repulsive forces between them and tetracycline molecules and thus competes for the active sites in the adsorbent, which is already limited. Therefore, the high percentage removal means that there are little competition and repulsion forces between tetracycline and hydroxide. In addition, the surface of the pomegranate peels will be ionized with positive hydrogen ions. This makes the adsorption process easier than if the number of hydroxide ions increases. This happens when the acidic function of the solution is raised.

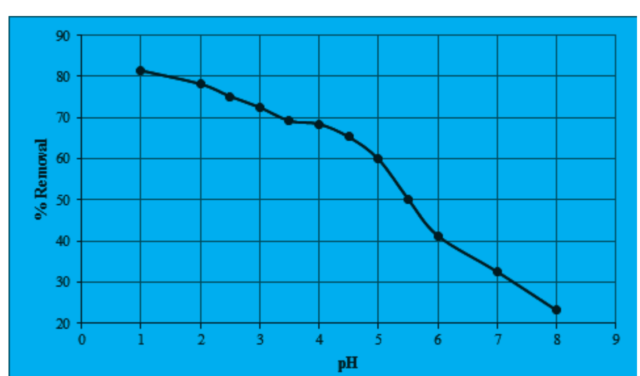

Figure 3 Effect of pH on the percentage removal of tetracycline antibiotic

3.3 Effect of Adsorbent Amount: The experimental results related to the study of the pomegranate peels effect as an adsorbent on the percentage of adsorption showed that the latter is increasing by increasing the amount of adsorbent by keeping the other operational parameters at optimum values. The maximum removal was recorded at the largest amount of adsorbent, which is 2.5 g, as shown in Figure 4. The direct correlation between the percentage of tetracycline removal and the amount of pomegranate peels is due to the fact that pomegranate peels have a specific surface area per unit weight. Increasing the amount of adsorbent will increase the surface area of the adsorption medium, which means more active sites, which in turn will provide a greater chance of adsorption of more molecules of tetracycline if the amount of pomegranate peels is less.

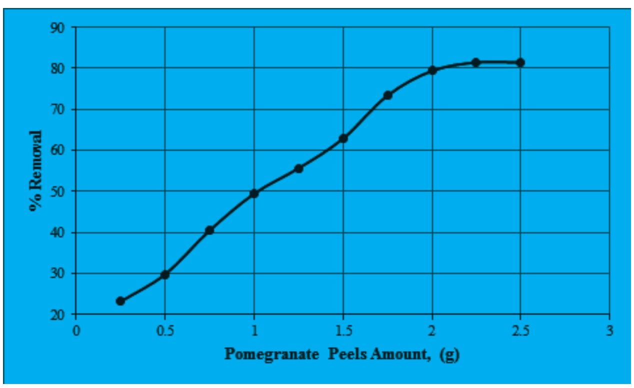

Figure 4 Effect of adsorbent media amount on the percentage removal of tetracycline antibiotic

3.4 Effect of Agitation Speed: The correlation between the percentage removal of tetracycline and different values of agitation speed is shown by Figure 5. Increasing the agitation speed will increase tetracycline removal for from aqueous solution using pomegranate peels as adsorption medium and keep the rest of the operational variables at optimal values. This results may be attributed for Increasing the agitation speed will reduce the thickness of the layer surrounding the adsorbent molecules, removing the surrounding obstacles and increasing the chance that tetracycline will bind to the active sites on the surface of the pomegranate peels, thus increasing the tetracycline removal from the aqueous solutions. This explanation is true up to the speed of 300 rpm, after this value the percentage removal remains constant and does never change whatever increasing the agitation speed. This may be due to the material is saturated with adsorbed molecules at optimum speed and that any increase in speed will not change the removal efficiency.

3.5 Effect of Contact Time: The increase in contact time leads to a corresponding increase in the percentage of tetracycline removal from aqueous solutions as shown in Figure 6, with keeping the rest of the operational variables at optimal values. Increasing the process time will increase the time when tetracycline molecules come into contact with pomegranate peels, which in turn will increase the chance of tetracycline binding to active sites on the surface of the adsorbent and thus increase the rate of antibiotic removal from aqueous solutions. If the time is less, vice versa, the adsorbent molecules do not find the time required to complete the adsorption process of the molecules of the contaminant and thus remain free in the solution, which leads to a decrease in the percentage of adsorption.

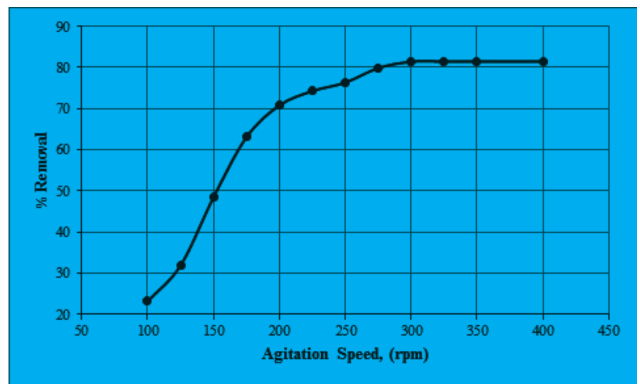

Figure 5 Effect of agitation speed on the percentage removal of tetracycline

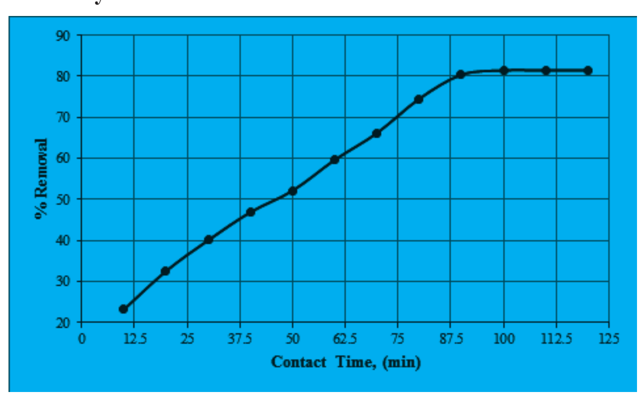

Figure 6 Effect of contact time on the percentage removal of tetracycline

4. Conclusions: From the results of the present study, the following conclusions can be drawn:

a. Adsorption technique showed high efficiency in the treatment of aqueous solutions contaminated with antibiotics in general and tetracycline in particular.

b. The maximum percentage removal was 81.46% at 1 ppm of the initial concentration of tetracycline, pH of 1, pomegranate peels amounts of 2.5 g, agitation speed of 300 rpm and contact time of 100 min.

c. Adsorption of tetracycline from aqueous solutions using pomegranate peels was directly proportional with the amount of adsorbent (pomegranate peels), agitation speed and contact time to a certain level and then constant. While the percentage removal was inversely proportional to the initial concentration of tetracycline and the pH of the aqueous solution.

Ethical Clearance: The Research Ethical Committee at scientific research by ethical approval of both environmental and health and higher education and scientific research ministries in Iraq

Conflict of Interest: The authors declare that they have no conflict of interest.

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