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Removal of Norfloxacin through Sulphonated Punica Granatum Outer Peels and Cow Dung - An Emerging Technique

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ABSTRACT

Due to the presence of antibiotics in water, the risks to human health and the environment as well as the associated financial losses have increased the urgency to develop effective and efficient technologies to thoroughly remove antibiotics from water. In the present study Pomegranate peels and cow dung mixture were used as a adsorbent and uptake of Norfloxacin was evaluated with different parameters like contact time, sorbent dose, and temperature. Results shows that sorption process is time, temperature and concentration dependant. Thus sulphonated mixture of biomass of Pomegranate peels and cow dung is a low cost and easily available good sorbent for the removal of Norfloxacin from wastewater.

Keywords: bioadsorption, effluents, Waste water, Norfloxacin

INTRODUCTION

In the modern world industrialization has brought about the development of new products but has generated contaminants also, which could play harmful role to our environment. In many developing countries the crisis of freshwater has been further damaged by pollutants from chemical and biological species, which have serious effects on human health. One of the most used classes of drugs in medical therapy is antibiotics, which have frequently been detected in surface and ground water. Most antibiotics cannot be fully absorbed and metabolized by humans and animals. Some of the antibiotics that are used excessively have low biodegradability and can potentially cause a variety of adverse effects including acute and chronic toxicity, disruption of aquatic photosynthetic organisms, impact on indigenous microbial populations, and damage to antibiotic-resistant genes in microorganisms. Thus, the presence of antibiotic residues in water is a major concern it poses serious risks to human and ecological system[1]. Norfloxacin is a synthetic antibacterial agent that belongs to the class of fluoroquinolone antibiotics. It is used to treat urinary tract infections, gynecological infections, inflammation of the prostate gland, gonorrhea and bladder infection.

The traditional water treatment systems used, only removes TDS and microorganisms from water but not completely effective in removing antibiotics. Hence, the risks to human health and the environment as well as the associated financial losses have increased the urgency to develop effective and efficient technologies to thoroughly remove antibiotics from water, in particular from drinking water[2].

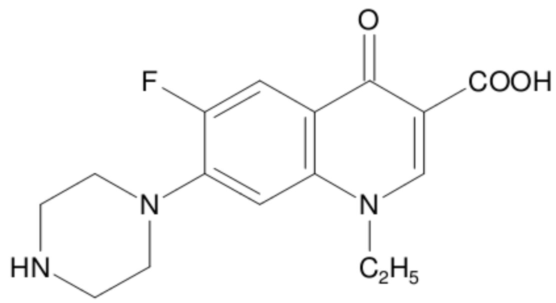

Figure 1. Structure of Norfloxacin

MATERIAL AND METHODOLOGY

Adsorbate preparation:

The antibiotic drug Norfloxacin (λmax = 300nm) was purchased from MERCK, INDIA. It was used without any improvisation or further purification. The drug solutions were prepared by dissolving appropriate amounts of drug in methanol and through bidistilled water, the different concentrations of the solutions 0.319 mg/L., 3.19 mg/L, and 31.9 mg/L. were prepared [3]

Adsorbent Preparation

Pomegranate outer peels and cow dung mixture were used as a adsorbent, which are abundantly available in the rural area in Chhattisgarh. Cow dung cakes were collected and dried at room temperature. The dried material of Pomegranate outer peels and cow dung were crushed, powdered and then soaked in AR conc. Sulphuric acid for 2 hours.[4] The biomass was then heated on a water bath till the fumes ceased then washed thoroughly with distilled water till the black mass was acid free. It was then dried at 110 ^{0}C in the oven for 3 hours and passed through 0.63 mm mesh to get particles of uniform size sorbent and stored in vacuum desiccators.

Adsorption study

The experiments is carried out in three sets and each set contain 50 mg of sorbent in different conical flasks, to each flasks 25 ml of freshly prepared. Norfloxacin solution of initial concentration was added. Although this concentration range is much higher than the antibiotics would be in most effluents, but high concentrations helped in minimizing the error in the estimation of drug spectrophotometrically. The volume was made up to 100 ml by adding distilled water. The flasks were protected from sunlight and stirred on magnetic stirrer with constant speed 400 rpm for sufficient time (5, 10, 15, 20, 25, 30,) minutes to achieve equilibrium and filtered through whatman filter paper. The absorbance of the filtrate was measured using systronic double beam spectrophotometer at 300 nm wavelength. The above mentioned process repeated to find the effect of different adsorption parameters like adsorbent dose, pH, contact time etc. by keeping all other parameters at a fixed value.[5,6] The dye uptake capacity for the adsorbate was calculated by simple concentration method.[7,8]

Where Qe is the quantity of sorbate (drug) uptake by biomass, Co and Ce are the initial and final concentrations respectively. V is the volume of solution in ml and m is the dry weight of the biomass added. The removal efficiency is calculated by,

$$Q_e = \left(\frac{C_o - C_e}{m}\right) V$$

Removal efficiency = $[(C_o - C_e)/ C_o] \times 100$

Where C_o is the initial concentration of drug, C_e is the drug solution concentration after adsorption at any time.[9,10]

RESULT AND DISCUSSION

Effect of contact time

It is shows that at all the concentrations of the drug, rate of adsorption is quite high and the process reaches equilibrium within 10 minutes. For an initial concentration of 0.319 mg/L the minimum amount adsorbed is 42% within 5 minutes and the maximum adsorption is 93.2% in 30 minutes. While for an initial concentration of 3.19 mg/L the minimum amount adsorbed is

48 % within 5 minutes and the maximum adsorption 94.1% within 30 minute. For an initial concentration of 31.9 mg/L the minimum amount adsorbed is 53 % within 5 minutes and the maximum adsorption 97.5% within 30 minute. Out of the total amount adsorbed at equilibrium, more than 60% is seen to be adsorbed within the initial 15 minutes itself (Figure 2).

Effect of Adsorbate concentration

Initial concentration affects the uptake capacity of the biosorbent to a large extent. (Figure 3) shows that adsorbent % increases with concentration of drugs. Adsorbent % increases from 42 to 53% as the concentration increases to 0.319 to 31.9 mg/L in same contact time. While maximum adsorption for 3.19 mg/L is found 94.1mg/L and for 31.9mg/L it is found 97.5%. Although fixed mass of sorbent can adsorb only a certain amount of drug, therefore larger the Sorbent mass, larger the amount of sorbate that can be removed. The concentration of the drug at the surface of the sorbent differs from that in the solution; there exists a concentration gradient in the solution & at the surface.

Effect of pH on adsorption

pH factor is one of the most important in controlling the adsorption process. To evaluate the effect of pH on the adsorption process, the adsorption of the drug with pH values from 2-9 were studied keeping all other variables constant. It was observed that (Figure 4) for the amount of drug adsorbed per unit weight of adsorbent (Qe) increased with decreasing pH values. Norfloxacin is acidic drug and exists in solutions as anionic form. Initially there is a competition for OH^- and anions, to attach to the adsorption sites However as pH decreases the number of OH^- ions in solution decreases till pH 4, and a slight increase is observed in % adsorption of the drug. As the pH increases to above 6, it is observed that the adsorption rapidly decreases. It became minimum at 9 pH.

Effect of Temperature on adsorption

To study the effect of temperature on adsorption experiments were carried out at three temperatures 25^0C, 35^0C and 45^0C using thermostat to maintain the temperature. The plots of %adsorption vs. time (fig. 5) indicates that maximum amount of drug are adsorbed at 45^0C. It shows that as the temperature increases the sorption capacities also increases The increase in sorption capacities with temperature indicates that with increasing temperature mobility of the (drug) ions increases. It can also be said that with rise in temperature the interaction between the dye molecules and the sorbent surface become more effective.

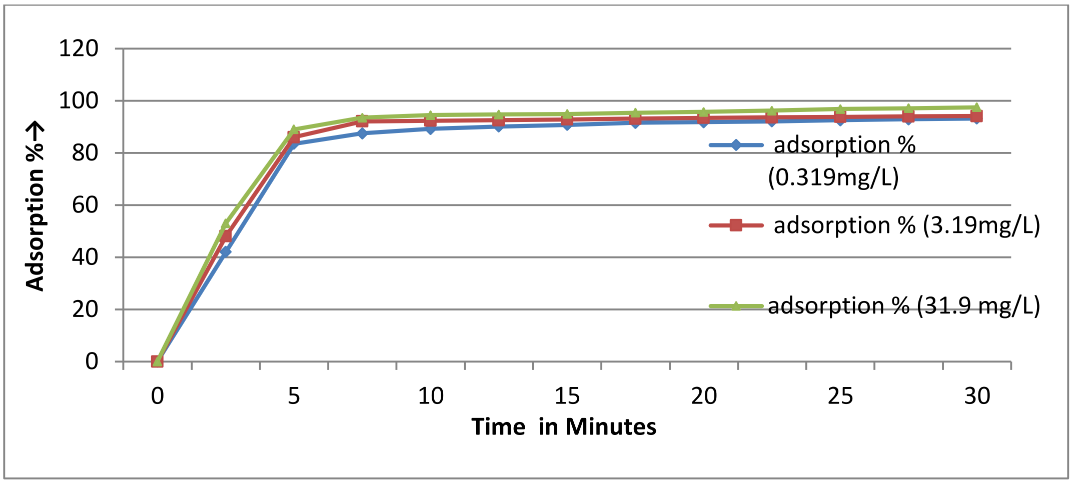

Figure 2 % Adsorption vs. contact time and different concentration of adsorbate

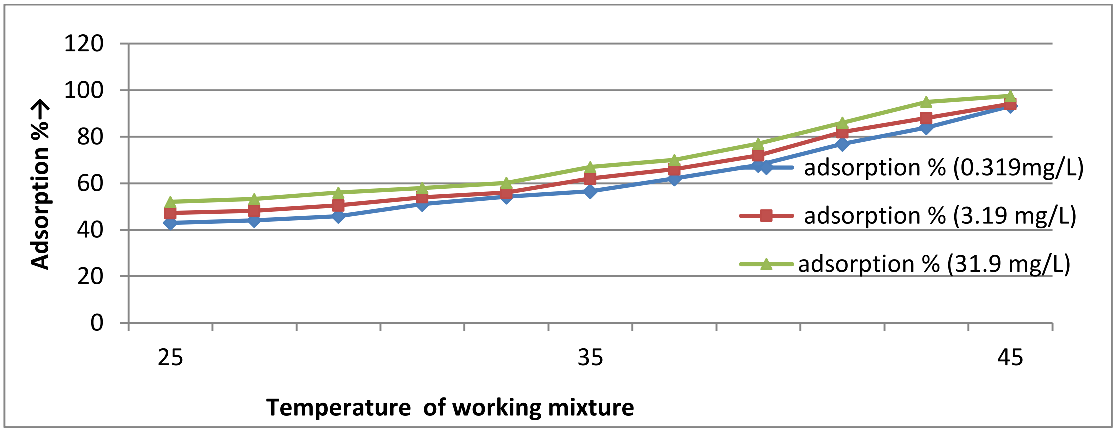

Figure 3. % Adsorption vs. temperature and different concentrations of adsorbate

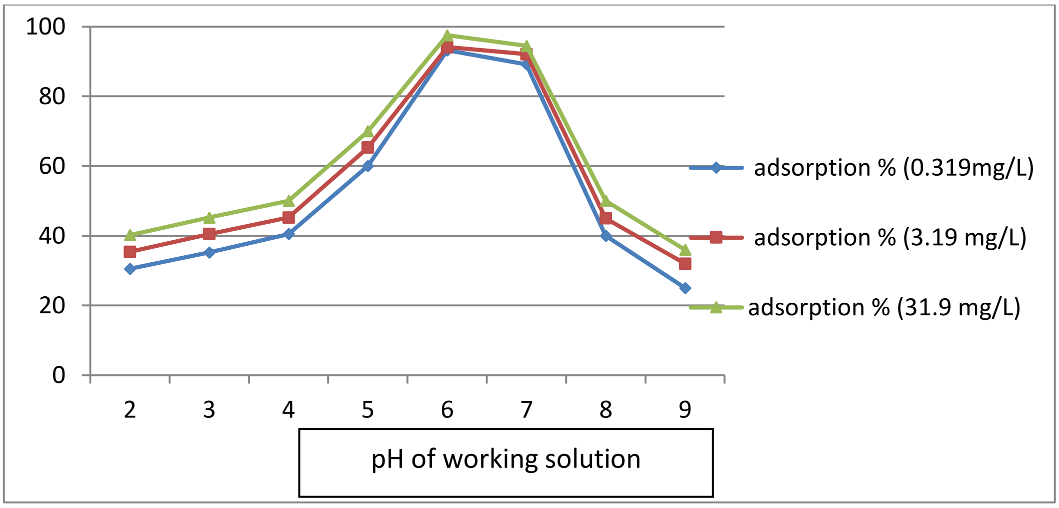

Figure 4. % Adsorption vs. pH in different concentration of adsorbate

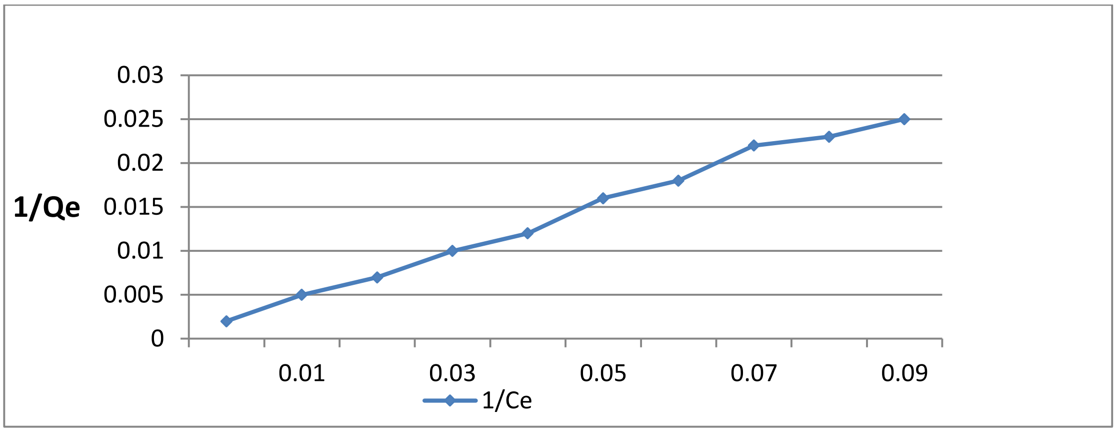

Figure 5. Langmuir adsorption isotherm of the adsorbents for Norfloxacin (Temperature = 45o ±1, rotations per minute=400±1, adsorbent dose= 31.9mg, equilibrium time = 30 minutes pH=6)

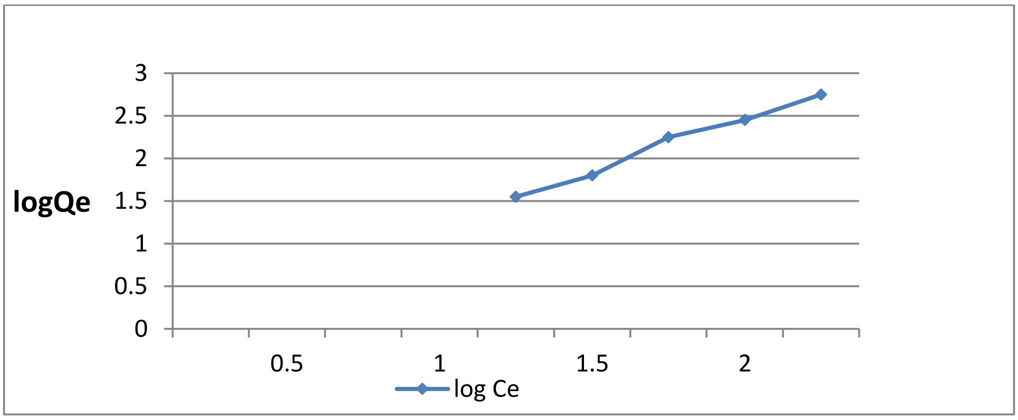

Figure 6. Freundlich adsorption isotherm of the adsorbents for Norfloxacin (Temperature = 45o ±1, rotations per minute=400±1, adsorbent dose= 31.9mg, equilibrium time = 30 minutes pH =6

Table 1. Langmuir and Freundlich constants for Norfloxacin

Parameter		Parameter	
Q_e (mg/g)	1095.2	KF	8.795
b (L/mg)	0.0490	n	1.520
R	0.870	R	0.790
RL	0.195		

CONCLUSION

Adsorption of Norfloxacin drug was investigated using two low cost bio waste adsorbents, sulphonated Punica Granatum outer peels and cow dung . It was found that adsorbent dose and initial concentration of drug has a significant effect on the adsorption of drug. It was concluded that pH of the solution has a marked effect on the adsorption and adsorption increased with the increase in pH till 6 then decreases and become minimum at 9 pH value. Both Langmuir and Freundlich adsorption isotherm fitted well for the adsorbent. Adsorption capacities were found to be 1095.2. It can be concluded that the mixture of pomegranate outer peels and cow dung can be used as adsorbents for the removal of antibiotic drugs like Norfloxacin.

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