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Ciprofloxacin Antibiotics Removal from Effluent Using Heat-acid Activated Red Mud

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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Original Research Article

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ABSTRACT

In this study, the adsorption of Ciprofloxacin (CIP) antibiotics from a synthetic solution containing CIP is investigated using Red Mud (RM) and Red Mud that is activated by HCL (ARM). Scanning Electron Microscopy (SEM) techniques are used to morphological characteristics of Red Mud and activated Red Mud. The optimum conditions for both absorbents obtained with the highest adsorption include contact time=90 min and adsorbent dosage= 4 g/L. The highest adsorption of CIP was 25.44 mg/g for Red Mud and for activated Red Mud was 41.5 mg/g. The negative value of the standard enthalpy change indicates that the adsorption is physical in nature involving weak forces of attraction and is also exothermic, thereby

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demonstrating that the process is stable energetically. The results of this study show that the activated Red Mud is a relatively effective adsorbent for the adsorption of cerium from aqueous solution.

Keywords: Red mud; ciprofloxacin; adsorption; temperature.

1. INTRODUCTION

Water contamination is caused by various sources such as industrial effluents, agricultural runoff and chemical spills [1-3]. Contamination of surface and even ground water is becoming an increasingly serious problem worldwide because of the growing population and wide use of chemicals, including pharmaceuticals [4,5]. Antibiotics have been used extensively in human and veterinary medicine. Most antibiotics are incompletely metabolized; thus, their residues and degradation products are excreted and can enter water environments in various ways [6,7]. About 30–90% of the given antibiotic dose can remain undegradable in the human or animal body and is largely excreted as an active compound [8]. Exposure to the residues and metabolites of antibiotics may cause a variety of adverse effects in the environment, such as antibiotics resistance of microorganisms and chronic and acute toxicity for organisms [9,10].

Ciprofloxacin (CIP) is a quinolone antibiotic widely used in livestock and poultry breeding industry because of its broad-spectrum antibacterial and efficiency [11]. Along with its popularization, various environmental problems also appear and have attracted more and more attentions from domestic and foreign scholars. However, current research on CIP mainly focuses on the clinical application of animal diseases, the animal in vivo pharmaco kinetics, drug residues in animal products, etc [12,13].

Thus, removal of antibiotics from water sources is particularly important. Various technologies and methods have been reported for antibiotics removal, including advanced oxidation, adsorption, photo degradation, and biodegradation [14,15]. Compared to other technologies, the adsorption process promises convenience, ease of operation, and simple design, and has been used for antibiotics removal [16]. In the present study, adsorption is proved to be a simple, economical and efficient method to remove antibiotics from wastewaters [17,18]. Various adsorbents have been explored for the adsorption of antibiotics, such as montmorillonite, biochar, activated carbon, carbon nanotubes, and goethite [19-22]. However, these adsorbents hold poor potential for antibiotics removals, such as low sorption capacities, high cost or poor regeneration performance [23,24].

The red mud is an inexpensive adsorbent which is widely used to treat the effluents. It is the most important residue of alumina production process. Bauxite stone has a large amount of aluminum hydroxide (Al_2O), so it is used in alumina production in Bayer process and red mud is produced waste of this process [25]. The aim of this study was using of red mud and modified red mud by HCL as an abundant and cheap adsorbent for Ciprofloxacin Antibiotics removal from aqueous solution.

2. MATERIALS AND METHODS

The RM sample used in this study was obtained from Tabriz Aluminum Industry Corporation, Iran. The chemical composition of RM is SiO_2, Fe_2O_3, Al_2O_3, CaO, MgO, K_2O and Na_2O. The RM is screened through a 100 mesh screen and dried at 105℃. RM was boiled in 0.5 M HCl solution for 2 h at 80℃, the ratio of liquid to solid was 20 mg/L. Finally, the acidified ARM samples were heated at 105℃ to get constant weight and stored in the valve bag for further study.

The surface morphology of RM before and after the modification was observed by a scanning electron microscopy performed using an FEI Quanta 200 electron microscopy.

Ciprofloxacin (CIP) antibiotics, ($C_{17}H_{18}FN_3O_3 \cdot HCl$, purity >98%) with a molecular weight of 696.6 g/mol was purchased from Sigma-Aldrich and used without further purification, the molecular structure of Ciprofloxacin is given in Fig. 1.

2.1 Adsorption Study

The ability of RM and ARM for removal of CIP from aqueous solutions was determined under batch mode conditions. The experiments were carried out in conical flasks by adding powdered

RM and ARM suspended in 100 mL of CIP solution at fixed pH (7) by gently agitating the solution in thermo statically orbital shaker at 200 rpm at a temperature and different contact time (10–150 min). At required contact time, the samples were filtered and the concentrations of RM and ARM in the filtrate were analyzed by a UV–Vis Spectrophotometer at a maximum wave length of 290 nm. The amount of CIP adsorbed onto RM and ARM was calculated based on the following [26-28]:

$$QE = \frac{V(C_0 - C_e)}{M}$$

Where QE is the maximum adsorption capacity in mg/g, C_0 is the initial concentration and C_e is the concentration at equilibrium of CIP solution in mg/L, V is the volume of the CIP solution in mL and m is the mass of the Adsorbent in gr.

Adsorption percentage (%) was derived from the difference of the initial concentration (C_0, mg/L) and the final one (C_e, mol/L) (Eq. 2) [29-31]:

$$\text{Sorption\%} = \frac{C_0 - C_e}{C_0} \times 100$$

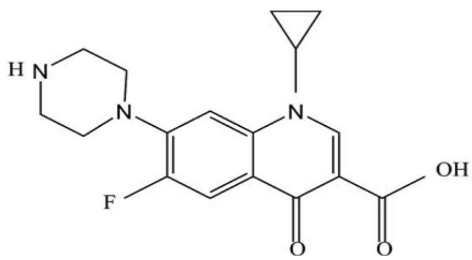

Fig. 1. The structure of ciprofloxacin

3. RESULTS AND DISCUSSION

3.1 Characterizations of ARM

The RM and ARM were observed by scanning electron microprobe at 10,000× magnification. The SEM images in Fig. 1 may provide visual evidence of the RM surface erosion and collapse. When RM was treated with HCl, the oxides of iron, calcium, sodium, and aluminum are converted to their respective chlorides. Calcium and some other acid-soluble salts were partially dissolved, and then some coarse exterior and new cavities appeared during the RM acidification process. The acidic surface treatments lead to the development of microspores or mesopores on the RM surface and create localized adsorption sites on the RM surface. It is the reason why the acidic treatment could result in a greater specific surface area and porosity.

3.2 Effect of Adsorbent Dosage

Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The effect of adsorbent has been studied on CIP removal and the results have been illustrated in Figs. 3 and 4. In general, the increase in adsorbent dosage increased the percent removal of adsorbate. As the adsorbent dosage was increased from 0.5 to 8 g, the CIP adsorption efficiency increased from 25.4% to 61.7% for RM (Fig. 3). Because the number of active sites increases with respect to increase of adsorbent dosage [32,33]. However, the CIP

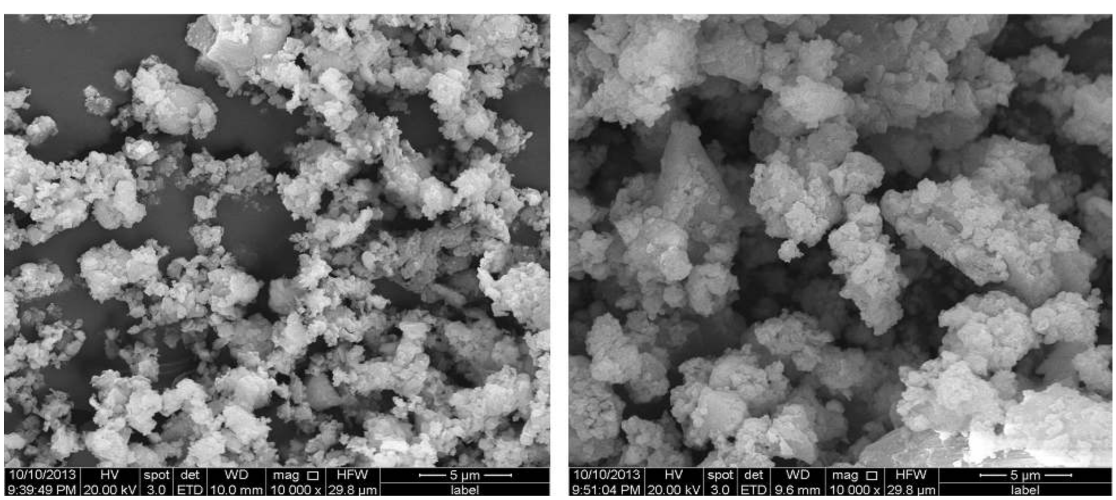

Fig. 2. SEM images of (a) RM and (b) RAM

adsorption efficiency was decreased when the adsorbent dosage was more than 4 g. Under the same conditions, the CIP maximum adsorption efficiency of ARM reached 98.29% (Fig. 4). This was because acid treatment RM can increase specific surface area and porosity [34-36]. Taking into account the above results, the dosage of CIP adsorption was set as 4 g in the following experiments.

3.3 Thermodynamic Parameters of Biosorption

The thermodynamic parameters reflect the feasibility and spontaneous nature of the process. Thermodynamic parameters such as free energy change, enthalpy change, and entropy change can be estimated using equilibrium constants changing with temperature [37]. Values of thermodynamic parameters are the actual indicators for practical application of a process. The amount of CIP adsorbed at equilibrium at different temperatures (273 to 323 K), have been examined to obtain thermodynamic parameters for the adsorption system. The thermodynamic parameters, change in the standard free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) associated with the adsorption process and these were determined using the following equations [38-40]:

$$\Delta G° = -RT \ln K$$

Where $\Delta G°$ is the standard free energy change, R is the universal gas constant (8.314 J/mol K), T the absolute temperature and K is the equilibrium constant. The apparent equilibrium constant of the sorption, K, is obtained from [41,42]:

$$K = \frac{C_i}{C_e}$$

Where K is the equilibrium constant, Ci is the amount of CIP adsorbed on the adsorbent of the solution at equilibrium (mg/L), Ce is the equilibrium concentration of CIP in the solution (mg/ L). K values were calculated at a different temperature to allow the determination of the thermodynamic equilibrium constant (K). The free energy changes are also calculated by using the following equations [43,44]:

$$\ln K = \frac{-\Delta G°}{RT}$$

$$\ln K = \frac{-\Delta H°}{RT} + \frac{\Delta S°}{R}$$

$\Delta H°$ and $\Delta S°$ were calculated from the slope and intercept of the van't Hoff plots of Ln K versus 1/T. The results are given in Table 1. The negative value of the standard enthalpy change (-9.25 and -7.64 kJ/mol for an ARM and RM respectively) indicates that the adsorption is physical in nature involving weak forces of attraction and is also exothermic, thereby demonstrating that the process is stable energetically [45]. The overall standard free energy change during the adsorption process

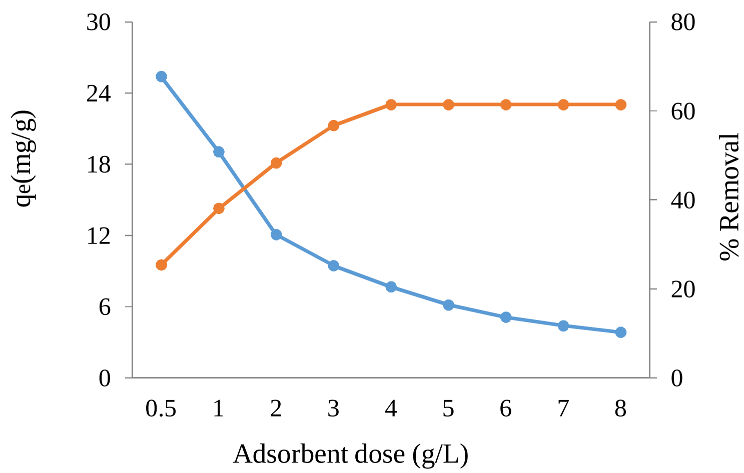

Fig. 3. Effect of adsorbent mass on adsorption of 50 mg /L CIP onto RM

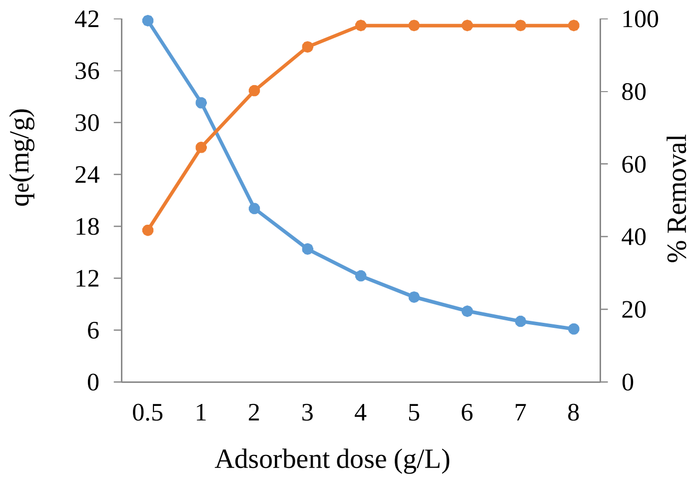

Fig. 4. Effect of adsorbent mass on adsorption of 50 mg /L CIP onto ARM

Table 1. Thermodynamic parameters for the adsorption of CIP onto RM and ARM

Temp (K)	ΔG°(KJ/mol)		ΔH°(KJ/mol)		ΔS°(KJ/mol)	
	RM	ARM	RM	ARM	RM	ARM
273	-0.27	-0.35				
283	-0.33	-0.46				
293	-0.39	-0.62	-7.64	-9.25	-0.76	-0.89
303	-0.48	-0.79				
313	-0.61	-0.91				
323	-0.73	-1.04				

was negative for the experimental range of temperatures corresponding to a spontaneous physical process of CIP adsorption and the system did not gain energy from an external source. When the temperature was increased from 273 to 323 K, the magnitude of the standard free energy change shifted to a low negative value, suggesting that the adsorption was rapid and more spontaneous at low temperature. The negative standard entropy changes (ΔS°) correspond to a decrease in the degree of freedom of the adsorption species.

4. CONCLUSION

In this study, the ability of RM and ARM for CIP removal from aqueous solution were studied. The amount of CIP removal was found to increase with increasing in adsorbent mass from 0. 5 to 4 g of RM and ARM. The thermodynamic constants of adsorption were also evaluated. The negative value of ΔG° confirms the spontaneous nature adsorption process. It can be concluded that the RM and ARM is an efficient adsorbent for the removal of CIP from aqueous solution can be used repeatedly.

CONSENT

It is not applicable.

ETHICAL APPROVAL

It is not applicable.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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