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STEEL PLANT MAGNETIC RESIDUE USED TO ADSORB AND REMOVE AMOXICILLIN FROM CONTAMINATED WATER - THERMODYNAMIC STUDY.

G.F. da Silva, L.C. Freitas , N. Ortiz

Institute for Nuclear and Energy Research , São Paulo - Brazil
Av.Professor Lineu Prestes, 2242 CEP: 05508-000
http://www.ipen.br ; nortiz@ipen.br

ABSTRACT: Antibiotics are specially designed to control bacteria infections in humans and veterinary medicine , their direct discharge in water resources can cause unpleasant odor, skin disorder, and develop microbial resistance. Amoxicillin is one of the most important commercial antibiotic in use due to high bacteria resistance and large spectrum against many microorganisms. However, the organic compound and its derivatives have to be removed after environmental discharge including raw domestic sewage. The adsorption techniques have to be improved to water treatment and wastewater reclamation, the studies include the determination of thermodynamic constants for adsorption process using magnetite substrate powdered with bentonite clay, the studies showed a considerable amoxicillin removal.

KEYWORDS: Amoxicillin; magnetite; bentonite clay; adsorption; thermodynamic study.

1. INTRODUCTION

The antibiotics discharge is a common occurrence and is considered a environmental risks to have in nature, and according to Leonard (2010) "The antibiotics are excreted in large quantities with more than 75% of them are being unmetabolized and are therefore likely to end up in domestic wastewater in significant quantities". The most common in use is amoxicillin which have been investigated and measured in several occasions including sewage treatment plants on different treatment levels. The adsorption process under laboratory conditions showed promising results in amoxicillin wastewater treatment in comparison with the traditional methods to treat pharmaceuticals discharge. In this project amoxicillin solution was treat with an adsorbent material main composed by steel plant slag, the magnetite was tailored as a magnetic substrate doped with bentonite clay by surface deposition. The substrate was prepared using powdered granules of magnetite with important magnetic properties, high surface area and large porous distribution. Those properties are very suitable for surface clay deposition and adsorption. The thermodynamics calculations was used to revealed if the process is spontaneous and confirmed by increasing the removal percentage while varying the temperature.

2. MATERIALS AND METHODS

The adsorbent used in the adsorption process was magnetite substrate which was treated with organophilic acid, the bentonite clay. The magnetite was collected as small particles in air filters, periodically cleaned and the resultant sludge was pumped to a press filter series. The cake (17 ton / day) with 26 % moisture was collected and characterized. The clay was added to the process to open the surface pores, to promote the organic affinity and improve the adsorption capacity to remove organic compounds and this process has been managed by an adsorption column treatment, where the bentonite clay passes through it afer a 50% dilution increase with deionized water to not alter the ideal pH of the treated material. The magnetite was saturated with acidic clay suspension and was dried until constant weight. The adsorption trials were performed at various temperatures, maintaining constant the mass of the adsorber material, and the concentration of the solution of amoxicillin. The experiment was performed in batch with constant temperature, pH and agitation. The adsorption process was controlled by the amoxicillin determination in different agitation intervals to compare the adsorption potential and the . The concentrations of amoxicillin in the process were determined after the constant time for centrifugation, and using VU-Vis spectrophotometry - Varian Cary 1E, the wavelengths of 273nm (standard method) and 195nm (characteristic of benzene groups).

3. EFFECT OF TEMPERATURE

The effect of temperature variation on the adsorption process of amoxicillin were studied at 23°C, 24˚C, 27˚C and 28˚C and 29°C when the other experimental parameters were kept constant. The adsorption processes showed increase efficiency with temperature increasing. The thermodynamic parameters associated with the sorption process such Gibb's free energy (ΔG°), enthalpy (ΔHº) and entropy (ΔSº) were evaluated from the given Equations:

$$\Delta G° = - R.T. \ln K_D \qquad (01)$$

$$\ln K_D = -\Delta G°/ R. T$$

$$\Delta G° = -\Delta H° + T \Delta S° \qquad (02)$$

Where: R is universal gas constant, T is the temperature in Kelvin (^{0}K) and $K_D = q_e/ C_e$ the adsorbate quantity for the adsorbent l/g .

Where: ΔG° is the Gibb's standard free energy
ΔH° - standard enthalpy;
ΔS° - the standard entropy;
R - the universal gas constant, 8.314 J/mol K;
T - the absolute temperature, K;
R^2 - the Pearson coefficient.

4. RESULTS AND DISCUSSIONS

The results revealed that the adsorption equilibrium decreased with the increase of temperature, the calculations were made using adsorption equilibrium constant. The thermodynamic studies are important to determine the effects of temperature on the adsorption. According with the line equation:

The experimental results indicate the line equation as follows:

$$\Delta G° = - 2{,}303 \times 8{,}314 \times T\ (10\text{-}3) \times \log Kc$$

$$y = 14{,}979 - 3{,}938x \qquad R^2 = 0{,}854$$

ΔS°= 14,979x 2,303x R = 14,979 x 2,303x 8,314

ΔS°= 286,80

ΔH°= 3,938x R x 2,303= 3,398x 8,314x 2,303

ΔH°= 75,40

The positive value of ΔH° indicates the adsorption reaction as endothermic process. The table 1 shows the ΔG° values obtained for adsorption process in different temperatures. The Figure 1 relates the standard free energy on different temperatures.

Table 1. Gibbs free energy calculations.

T(K)	**X**= 1/ T x 10^{-3}	**log Kc**	**ΔG°** (KJ/mol)
302	3,31	2,0	-11,56
301	3,32	1,90	-10,95
300	3,33	1,81	-10,40
297	3,37	1,62	-9,21
296	3,38	1,76	-9,97

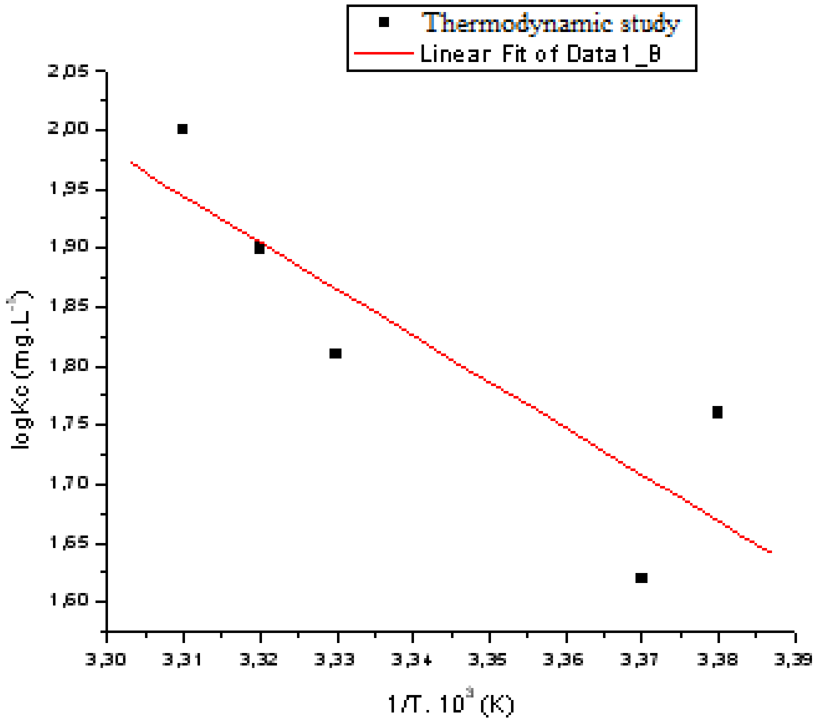

Figure 1. Thermodynamic calculations for amoxicillin adsorption system.

The thermodynamic studies were obtained by the results based on the analysis of the variation of the concentration of the antibiotic solution regarding its potential to reduction after the process caused by the absorbent in the entire system. The previous calculation, including the axes priority, was kept by the analysis of the following parameters varying with the system temperature:

Ci = Initial concentration

Ce= Amount of metal by mass of adsorbent retained material after the equilibration time

$C_{ac=}$ Relative concentration difference

Kc= Thermodynamic equilibrium constant in ratio to the concentrations.

T(K)	**Ci(g/L)**	**Ce(g/L)**	**C_{ac}(g/L)**	**Kc(10^{-3})**	**Y=logKc**
302	0,08754	0,07957	0,00797	100,2	2,00
301	0,08754	0,08116	0,00638	78,6	1,90
300	0,08382	0,07877	0,00550	64,1	1,81
297	0,08674	0,08329	0,00345	41,4	1,62
296	0,08275	0,07824	0,00451	57,6	1,76

Table 2. Thermodynamic constants for calculations bases

Proven results for the calculation of the thermodynamic constants for the adsorption of the antibiotic depending on the adsorption temperature study obtained, all of them starting from the same initial concentrations and with an appreciated result relatively constant for a given change in the temperature.

Table 3. Thermodynamic constants published for adsorption experiments using magnetite as absorber material.

Sources	Gibbs free energy ΔG°	Entropy ΔS°	Enthalpy ΔH°
EXPERIMENT Magnetite to treat and adsorb amoxicillin	-11,5 kJ/mol	286,80 kJ/mol.K	75,40 kJ/mol
Roonasi P[1], Holmgren A.(2009) e Kara A. and Dermibel E.(2011)	ATR-FTIR study of sulphate sorption on magnetite, rate of adsorption -33,3 kJ/mol	Characterization of Magnetic-Poly(divinylbenzene-vinylimidazole) Microbeads 77.40 kJ/mol.K	Characterization of Magnetic-Poly(divinylbenzene-vinylimidazole) Microbeads 8.655 kJ/mol
Chowdhury, S. R. et al (2010)	Arsenic removal from aqueous solutions by mixed by magnetite–maghemite nanoparticles -35 kJ/mol	NR*	NR
Lin, Y.-F., Chen, H.-W., et al. (2011)	Application of magnetite modified with aluminum/silica to adsorb phosphate in aqueous solution - 21,47 kJ/mol	NR	NR

***NR**= not referenced

The values obtained for ΔH and ΔG show that the adsorption process is endothermic on the activated adsorption, the characteristic behavior of adsorption with chemical and physical characteristics, when the predominant characteristics of the chemical adsorption temperature increase and the entropy of the system gets higher, facilitating the contact between the molecules and the adsorption in the range of 296 and 302K. The enthalpy and the entropy values are important to identify the thermodynamic behavior. They have been tabulated and published as a requirement for a variety of applications. The Table 3 shows the comparison of thermodynamics results with those published. The entropy, free energy, and enthalpy were in the range of published values. This effect is an evidence of the high efficiency of the use of steel works slag as adsorbent material after surface clay treatment.

5. CONCLUSION

The magnetite collected as steel plant sludge can be prepared with acid organophilic clay and used as adsorbent material to treat and remove amoxicillin from contaminated water. The experimental data allows the thermodynamics calculations and the obtained results were in the range of those found in literature for magnetite. The process was confirmed as a the possibility of the use of low cost adsorbent, to treat and remove the pharmaceutical compounds from sewage treatment plant and domestic sewage discharge.

6. REFERENCES

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7. ACKNOWLEDGMENT

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