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Biosorption of Ranitidine Onto Live Activated Sludge

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Ranitidine is a drug responsible for disturbing the microbial ecology of surface waters. The potential use of live activated sludge (0.5 g and 1.0 g) for removal of ranitidine, one of the most widely used H_2-receptor antagonists, from aqueous solution was examined. The biosorption of ranitidine on live activated sludge was investigated in a batch system. The ranitidine biosorption was fast and equilibrium was attained within 10 min. Data obtained from batch studies applied to Langmuir, Freundlich, Tempkin isotherm models. Kinetic and equilibrium adsorption data show that the process obeys to the pseudo-second order kinetic equation, Freundlich and Tempkin adsorption models. Gibbs free energy values were found to be 4.588 kj/mol for 0.5 g adsorbent and 3.613 kj/mol for 1.0 g adsorbent and indicating the not spontaneity of the system. Octanol-water partition coefficient (K_{ow}) and biosorption coefficient, K_d, which describes the solid liquid partitioning characteristics of a compound in biosorption mechanism were also calculated.

Key Words: Ranitidine, Biosorption, Activated sludge, Adsorption kinetics, Thermodynamic parameters.

INTRODUCTION

Presence of pharmaceuticals and their metabolites in the aquatic environment has been recognized as the one of the most important issues in environmental chemistry. Many of the pharmaceuticals applied in human medical care are not completely eliminated in the human body. They unchanged mostly conjugated to polar molecules. These conjugates can be released into the aquatic environment by effluents from wastewater treatment plants. According to the previous studies that the pharmaceuticals and their metabolites entering water supplies and the food chain may pose a real threat, both to the ecosystem and to human health[1,2].

The pharmaceuticals were detected in low concentrations in many countries in environmental samples all around the world. Low levels of these pharmaceuticals have been detected in many countries in wastewater treatment plants effluents, surface water, groundwaters, drinking waters, seawaters and river waters.

According to Garrison *et al.*[3], the occurance of pharmaceuticals was first reported that it detected clofibric acid in treated wastewater in the USA at concentrations from 0.8 to 2 µg/L. Following these study, it has been detected more than 80 pharmaceuticals in aquatic environment in Canada, Spain, England, Italy, Sweden and Australia[2]. In recent years, presence of the pharmaceuticals in environment increased due to development of new analytical techniques.

Nowadays, physical, chemical, biological methods and advance treatment methods are applied to wastewater treatment. Solid content of wastewater is removed in primary treatment step. Secondary treatment includes biological systems and organic materials are removed in this step. On the other hand, abiotic losses plays an important role for wastewater treatment. In some cases, it may be more important than biodegradation[4-7]. Abiotic losses includes hydrolysis, photolysis, volatility and adsorption. The adsorption plays an important role constitute of basic step of biological degradation. If the organic matter adsorb by activated sludge, it can be biological degradable[8-10].

Adsorption is a well powerful technique for treating domestic and industrial effluents. According to Aksu and Tunc[11], becteria, yeasts, fungi and algae have special surface properties and enable them to adsorb different kinds of organic and inorganic pollutions from solutions. Biosorption is used to demonstrate a number of metabolism-independent processes (physical and chemical adsorption, electrostatic interaction, ion exchange, complexation, chelation and microprecipitation) occuring in the cell wall.

Ranitidine is one of the most consumed pharmaceuticals all over the world. In Australia (1998) annual consuption of Ranitidine is 33.7 t/year, in England (2000) 36.32 t/year; in Germany (2001) 85.81 t/year; in Italy (2001) 26.67 t/year and in Switzerland (2004) 1.60 t/year[12]. It is a specific H_2 receptor antagonist drug widely used in treatment of heartburn and in

healing ulcer. Being soluble in water it is readily soluble in organic solvents.

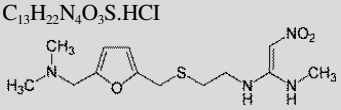
The objective of our paper is to determine adsorption properties of ranitidine-live sludge system. In this way, kinetic and equilibrium biosorption data were obtained and the effect of several sludge dose (0.5 g and 1.0 g) in the biosorption process was evaluated.

EXPERIMENTAL

Preparation of biosorbent: The activated sludge was collected from the full scale activated sludge plant of Pepsi Soft Drink Filling Industry, Adana, Turkey. The biosorbent was used on the same day as it was sampled. Total suspended solids were measured by the standard gravimetric technique[13].

Preparation of ranitidine solutions for biosorption: Test solutions containing ranitidine were prepared by fresh stock ranitidine solution which was obtained by dissolving weighed quantity of ranitidine salt (crystalline form purchased from Fako Actavis Company, Turkey) in methanol and distilled water. Some physical and chemical properties of ranitidine used in this work are summarized in Table-1.

TABLE-1
SOME PHYSICAL AND CHEMICAL PROPERTIES OF RANITIDINE

Drug class	H_2 Receptor Antagonist
CAS Number	66357–59–3
Chemical name	N[2-[[[5-[(dimethylamin) methyl]-2-furanyl] Methyl] ethyl]–*N*- methyl-2-nitro-1,1ethanediamin
Chemical Formula	$C_{13}H_{22}N_4O_3S.HCI$
Structural formula	
Molecular weight (g/mol)	350.87
Solubility in water (mg/L)	
Melting point (ºC)	133-135
Plasma half life [h]	2-3
UV Spectrums (wavelength) (λ_{max}) nm	229
Solubility	Soluble in water and methanol
Physical appearances	White crystalline dust
Odour	Odourless

Batch studies: The sorption tests were conducted in a routine manner by a batch technique at 25 ºC. The activated sludge (62.50 mL) was added to aqueous soluions (62.50 mL) of ranitidine. Volume of final mixture was adjusted to 125 mL containing 4000 mg/L activated sludge (0.5 g).

According to second study the activated sludge (125 mL) was added to aqueous (125 mL) of ranitidine. Volume of final mixture was adjusted to 250 mL containing 4000 mg/L activated sludge (1.0 g).

The data for deriving the isotherms constant were obtained by using sludge (0.5 g and 1.0 g) and ranitidine concentrations of 25, 50, 100 and 200 mg/L. The contact time was 160 min. Before analysis the samples were centrufuged at 6000 rpm for 20 min and the supernatant liquid was analyzed for the remaining ranitidine. All the experiments were carried out in duplicates.

Analysis of the concentration of ranitidine: The final concentration of ranitidine in solution was measured using an UV-VIS spectrophotometer Perkin Elmer at a wavelength of 229 nm. The amount of ranitidine biosorbet onto activated sludge biosorbent, q_e (mg g^{-1}), was calculated by a mass balance relationship as follows:

$$q_e = (C_0\text{-}C_e)\ V/W$$

where, C_0 and C_e are the initial and equilibrium liquid-phase concentration of ranitidine, respectively (mg L^{-1}), V the volume of the solution (l) and W is the dry weight (g) of activated sludge.

RESULTS AND DISCUSSION

Specific adsorption results are shown in Figs. 1 and 2 for various ranitidine concentrations for 160 min. Results showed that equilibrium was reached for almost 10 min. Möhle *et al.*[14] carried out a research on adsorption of some pharmaceuticals by activated sludge in batch activated sludge reactor and reported that adsorption process was fast and completed with in about 20 min. Results obtained from this current work within good agreements with the findings of Möhle *et al.*[14].

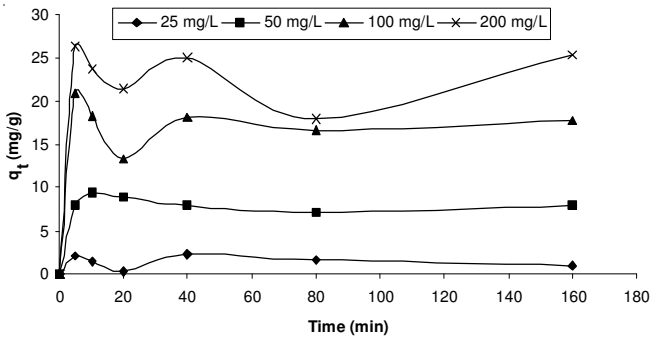


Fig. 1. Changing of specific adsorption results for various ranitidine concentration (0.5 g adsorbent)

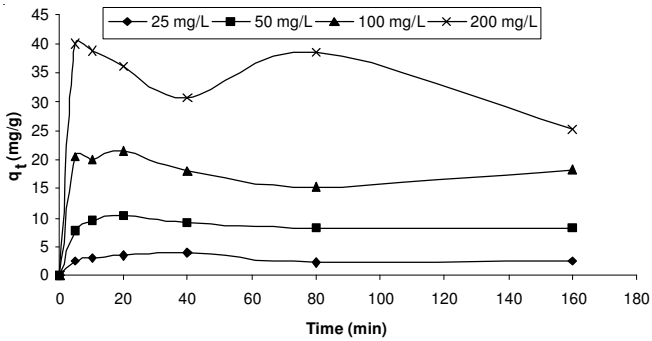


Fig. 2. Changing of specific adsorption results for various ranitidine concentration (1.0 g adsorbent)

The equilibrium adsorption isotherm is fundamentally important in the design of adsorption system. Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms. By plotting solid phase concentration (mg/g) against liquid phase concentration (mg/L) graphically it is possible to depict the equilibrium adsorption isotherms. [15]. In all models C_e is the equilibrium concentration of ranitidine solution after biosorption (mg/L), q_e is the equilibrium solid phase concentration (mg/g).

Tables 3 and 4 showed that 0.5-1.0 g of sorbent used and the low correlation coeeficient were obtained from Langmuir isotherm models and values of Q_{max} were also found negative. This negative value was also reported by Robinson *et al.*[16], which indicate that Langmuir model was not sufficient to describe this dye plant sorption system.

Determination of thermodynamic parameters: It is well known fact that thermodynamic parameters such as enthalpy change (ΔH), free energy change (ΔG) and entropy change (ΔS) can be estimated by using equilibrium constants changing with temperature. Gibbs free energy (ΔG) from the calculated following equation:

$$\Delta G = -RT \ln K_c$$

where, K_c is the equilibrium constant; R is the universal gas constant 8.314 J/mol K and T is absolute temperature K. The free energy change indicates the degree of spontaneity of the adsorption process[17]. The equilibrium constant of biosorption is defined as:

$$K_c = C_a/C_e$$

where, C_a is the solid phase concentration in equilibrium (mg/L), C_e is the equilibrium concentration in solution (mg/L). The free energy change can be represented as follows:

$$\Delta G = \Delta H - T\Delta S$$

According to equilibrium a plot of free energy change *versus* temperature (K) is linear and the enthalpy and entropy change values are determined from the slope and intercept of the plot[18].

According to Table-2, the free energy changes for ranitidine (0.5 g sorbent and 1.0 g sorbent) biosorption processes were obtained as 4.588 and 3.613 kj/mol at 298 K respectively. The possitive values of ΔG shows that the biosorption of ranitidine on live activated sludge endotermic in nature.

Determination of sorption coefficients for ranitidine: Biosorption is caused by electrostatic interactions and absorption by hydrophobic properties. Sorption ability can be estimated from the sorption coefficient (K_d) that mainly depends on the properties of the both ranitidine and sludge. Following equation is given for the calculation of K_d; $K_d = q_e/C_e$ where; q_e is the equilibrium solid phase concentration (mg/g) and C_e is the equilibrium concentration of ranitidine in solution after biosorption (mg/L) and K_d sorption coefficient (L/g). Several studies report expressions where K_d is estimated direcly from the octanol-water partition coefficient (K_{ow}). Octanol-water partitioning coefficient can be calculated using following equation. $K_{ow} = C_o/C_w$ where; C_o : concentration of compounds at octanol phase (mg/L), C_w : concentration of compounds at water phase (mg/L).

The effectiveness of sorption can be stated using the octanol water partition coefficient (K_{ow})[19].

1) If log K_{ow} is less than 2.5, the compound has a low adsorption potential.

2) If log K_{ow} is between 2.5 and 4 the compound has a medium adsorption potential.

3) If log K_{ow} is more than 4, the compound has a high adsorption potential.

TABLE-2
COMPARISON OF GIBBS FREE ENERGY VALUES FOR VARIOUS SYSTEM

Sorbent	Drug	ΔG (kj/mol)	T (K)
Activated sludge (0.5 g) (Present work)	Ranitidine	4.588	298
Activated sludge (1.0 g) (Present work)	Ranitidine	3.613	298
Kaolin (0.25 g)[1]	Metmorfin HCl	3.43	310.50
Attapuligate (0.25 g)[1]	Metmorfin HCl	1.017	310.50

TABLE-3
K_d VALUES (0.5 g SORBENT)

Initial concentrations (mg/L)	K_d (L kg^{-1})	K_d (average)
25	42.260	158.556
50	202.240	
100	236.323	
200	153.401	

TABLE-4
K_d VALUES (1.0 g SORBENT)

Initial concentrations (mg/L)	K_d (L kg^{-1})	K_d (average)
25	116.763	140.759
50	206.188	
100	240.085	
200	151.139	

TABLE-5
EQUATIONS DEVELOPED BASED ON RELATIONS BETWEEN K_d AND K_{ow}

Equations	References
$\log K_d = 0.58 \log K_{ow} + 1.14$	20
$K_d = 0.39 + 0.67\ K_{ow}$	21
$K_d = 0.33453 * K_{ow}$	22
$K_d = 0.1435 * K_{ow}$	23

TABLE-6
VALUES OF K_{ow} AND log K_{ow}

System	$\log K_d = 0.58 \log K_{ow} + 1.14$		$K_d = 0.39+0.67\ K_{ow}$		$K_d = 0.33453*K_{ow}$		$K_d = 0.1435*K_{ow}$	
	K_{ow}	log K_{ow}	K_{ow}	log K_{ow}	K_{ow}	log K_{ow}	K_{ow}	log K_{ow}
Ranitidine-activated sludge (0.5 g)	7.464	0.873	62.492	1.795	126.3	2.101	294.4	2.469
	102.329	2.010	301.26	2.478	604.5	2.781	1409	3.149
	133.659	2.126	352.13	2.546	706.4	2.849	1646	3.216
	63.533	1.803	228.37	2.358	458.5	2.661	1068	3.028
Average	**67.142**	**1.827**	**236.06**	**2.373**	**473.9**	**2.675**	**1104**	**3.043**
Ranitidine-activated sludge (1.0 g)	39.627	1.598	173.69	2.239	349.0	2.542	813.6	2.910
	105.681	2.024	307.16	2.487	616.3	2.789	1436	3.157
	137.404	2.138	357.75	2.553	717.6	2.855	1673	3.223
	61.944	1.792	224.99	2.352	451.7	2.654	1053	3.022
Average	**54.701**	**1.738**	**209.50**	**2.321**	**420.7**	**2.624**	**980.8**	**2.991**

TABLE-7
PARAMETERS OBTAINED FROM THE ISOTHERM MODELS FOR RANITIDINE BIOSORPTION (0.5 g)

Isotherm	Parameters	Values	Equations
Freundlich	n	0.645	y = 1.548x-1.8443
	K_f (mg/g)(L/mg)$^{1/n}$	-0.01431	
	r	0.899	
Langmuir 1	q_m (mg/g)	-14.422	y = -0.0694x+15.101
	K_a (L/mg)	0.0662	
	r	0.4746	
Langmuir 2	q_m (mg/g)	-3.721	y = 26.346x-0.2687
	K_a (L/mg)	-0.0102	
	r	0.899	
Langmuir 3	q_m (mg/g)	2.0669	y =68.994x+2.0669
	K_a (L/mg)	-0.0144	
	r	0.544	
Langmuir 4	q_m (mg/g)	23.860	y = 0.0043x+0.1026
	K_a (L/mg)	-0.0043	
	r	0.544	
Tempkin	B	12.674	y = 12.674x-38.5
	K_T	0.0047	
	r	0.994	

TABLE-8
PARAMETERS OBTAINED FROM THE ISOTHERM MODELS FOR RANITIDINE BIOSORPTION (1.0 g)

Isotherm	Parameters	Values	Equations
Freundlich	n	0.897	y =1.1143x-0.9656
	K_f (mg/g)(L/mg)$^{1/n}$	0.108	
	r	0.954	
Langmuir 1	q_m (mg/g)	-303.0303	y = -0.0033x+6.2968
	K_a (L/mg)	0.158	
	r	0.1072	
Langmuir 2	q_m (mg/g)	-18.867	y = 9.0887x-0.053
	K_a (L/mg)	-0.00583	
	r	0.966	
Langmuir 3	q_m (mg/g)	3.7529	y =54.534x+3.7529
	K_a (L/mg)	-0.0183	
	r	0.296	
Langmuir 4	q_m (mg/g)	-97.937	y = 0.0016x+0.1567
	K_a (L/mg)	-0.0016	
	r	0.296	
Tempkin	B	11.475	y = 11.475-32.945
	K_T	0.056	
	r	0.993	

Conclusion

The equilibrium and kinetic analysis of the biosorption of ranitidine on live activated sludge has been investigated. Ranitidine was adsorbed by activated sludge to some degree. Adsorption was fast and completed with in 10 min. The Langmuir, Freundlich and Tempkin isotherm models were applied to the equilibrium data. It was observed that the biosorption data of ranitidine fitted well to Freundlich and Tempkin isotherm models than the others. Determination of thermodynamic parameters as enthalpy, entropy and Gibbs free energy changes showed the irreversible and endothermic nature of the biosorption of ranitidine by live activated sludge. Based on the K_d and K_{ow} values, it is suggested that the biosorption of ranitidine by live activated sludge was not high.

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