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Investigation of the Veterinary Drug Adsorption Characteristics by Live Activated Sludge

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Abstract. In this paper, the adsorption properties of activated sludge, for a veterinary drug of ivermectin were investigated as a biosorbent and the results were compared with other biosorbents. The adsorption properties of the activated sludge (0.5 g and 1.0 g) on pharmaceutical that is ivermectin has been investigated. The drug biosorption was fast and equilibrium was attained within 20 minutes. The Langmuir and Freundlich isotherms models were applied to the experimental data and isotherm constants were calculated. High correlation coefficient with Langmuir Model was observed, however, negative Qmax value was observed indicating the inadequacy of Langmuir model. High correlation coefficient was also obtained with application of Freundlich model and it was found more suitable for the activated sludge system. Gibbs free energy values (ΔG=0.997 kj/mol for 0.5 g; ΔG=4.720 for 1.0 g) were calculated and it is concluded that the biosorption of ivermectin from aquatic solution on live activated sludge was endotermic in nature.

Keywords: Biosorption, veterinary drug, activated sludge

1. Introduction

Occurance of veterinary pharmaceuticals is recognized as an important issue in the field of environmental chemistry. Many tones of human and veterinary pharmaceuticals are sold in Turkey every year. Approximatelly 4000 different human and veterinary pharmaceutical active compounds are susceptible to reach every environmental compartment in Europe [1]. They help to protect the health and to ensure to well being of not only humans but also animals.

Veterinary pharmaceuticals (VPs) are used in large amounts in modern husbandry. Occurence, transport and fate of veterinary pharmaceuticals in the environment has recently increased. Agricultural livestock applications are the primary sources of pharmaceuticals in the environment. Veterinary pharmaceuticals used in animal feeding operations or as injections are released to the environment with animal wastes through direct deposition, discharge from treatment facilities, overflow or leakage from storage structures, or via direct land application [2], [3]

Most of veterinary pharmaceuticals contain synthetic bioactive compounds which are not easy to break down by the environment. They can escape degradation, and eventually they can contribute to widespread environmental pollution. They may be degraded by biotic and abiotic processes. These processes include not only hydrolysis but also photolysis [4], [5]

The biosorption technique has been used wastewater treatment and removing pharmaceuticals from aquatic solutions. If a sorbent is inexpensive and ready for use, the biosorption process will be a promising technique. Recently, a few materials had been used as sorbents for removal of pharmaceuticals from aqueous solution, which included homo-ionic clay [6], *Rhizopus arrhizus*, activated carbon and dry activated sludge [7]; tea leaves [8]; chitosan [9]; attpuligate and kaolin [10].

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The objective of this research is to determine adsorption properties of ivermectin-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.

2. Materials and Methods

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 (TSS) were measured by the standard gravimetric technique [11]. Test solutions containing ivermectin were prepared by fresh stock ivermectin solution which was obtained by dissolving weighed quantity of ivermectin in methanol and distilled water.

The sorption tests were conducted in a routine manner by a batch technique at 25 ^{0}C. The activated sludge (62.50 ml) was added to aqueous soluions (62.50 ml) of ivermectin. Volume of final mix 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 ivermectin. Volume of final mix 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 ivermectin 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 analysed for the remaining ivermectin. All the experiments were carried out in duplicates. The final concentration of ivermectin in solution was measured using an UV-Vis spectrophotometer Perkin Elmer at a wavelength of 200 nm. The amount of ivermectin biosorbet onto activated sludge biosorbent, qe (mg g^{-1}), was calculated by a mass balance relationship as follows:

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

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

3. Results

Initial biosorption tests showed activated sludge adsorbed ivermectin (Fig. 1 and Fig. 2). The data also showed that significant biosorption occurs 20 min; however 1 h was chosen to achieved to equilibrium. After these initial experiments, further adsorption tests were carried out. Table 1 showed that applied isotherm models and their linear forms. The Parameters Obtained from the Isotherm models for Ivermectin Biosorption showed that Table 2 and Table 3.

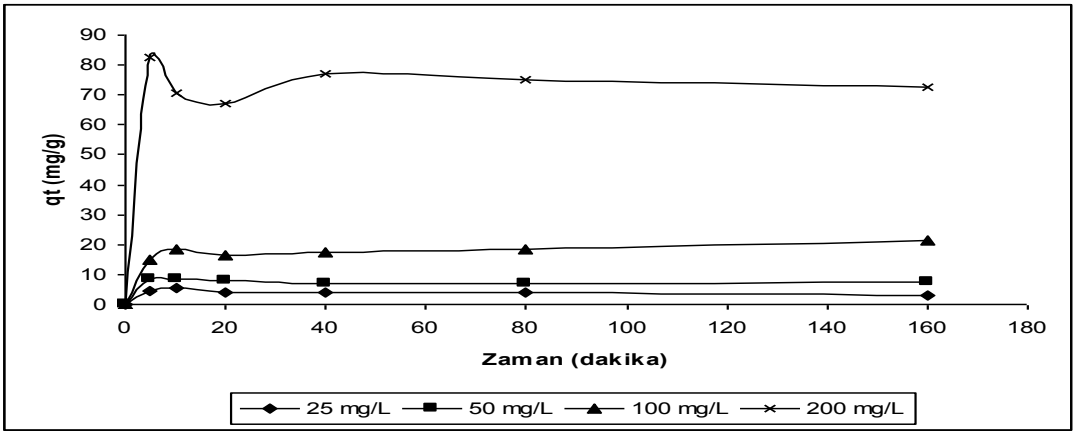

Fig. 1: Changing of specific adsorption results for various ivermectin concentration (0.5 g adsorbent)

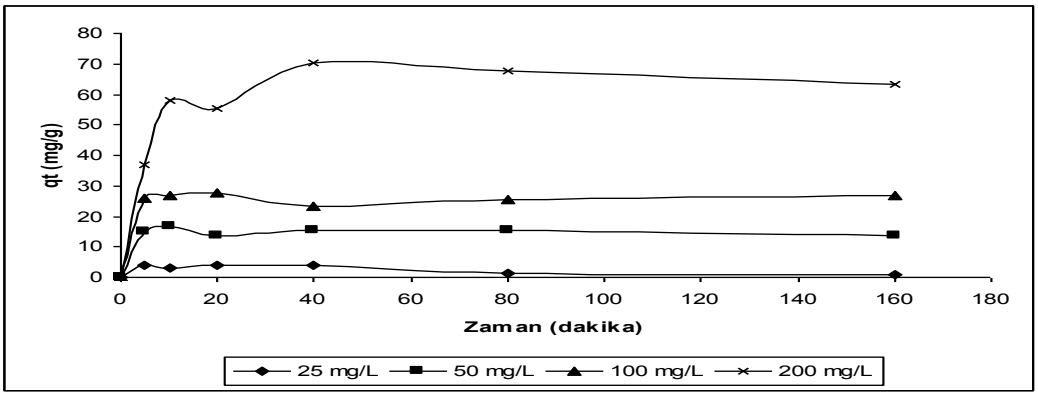

Fig. 2: Changing of specific adsorption results for various ivermectin concentration (1.0 g adsorbent)

Table 1: Applied isotherm models and their linear forms

Isotherm		Linear form	Plot
Langmuir 1	$qe = \frac{q_m K_a C_e}{1 + K_a C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m}$	$\frac{C_e}{q_e}$ vs. C_e
Langmuir 2		$\frac{1}{q_e} = \left(\frac{1}{K_a q_m}\right)\frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e}$ vs. $\frac{1}{C_e}$
Langmuir 3		$q_e = q_m - \left(\frac{1}{K_a}\right)\frac{q_e}{C_e}$	q_e vs. $\frac{q_e}{C_e}$
Langmuir 4		$\frac{q_e}{C_e} = K_a q_m - K_a q_e$	$\frac{q_e}{C_e}$ vs. q_e
Freundlich	$qe = K_f C_e^{1/n}$	$\log(q_e) = \log(K_f) + 1/n \log(C_e)$	$\log(q_e)$ vs. $\log(C_e)$

Table 2: The Parameters Obtained From The Isotherm Models For Ivermectin Biosorption (0.5 g)

Isotherm	Parameters	Values	Equations
Freundlich	N	0.521	y =1.9165-2.0933
	K_f(mg/g)(L/mg)$^{1/n}$	0.00806	
	R	0.978	
Langmuir 1	q_m(mg/g)	-15.408	y = -0.0649+7.8149
	K_a (L/mg)	0.127	
	R	0.9989	
Langmuir 2	q_m(mg/g)	-15.128	y =7.8713x-0.0661
	K_a (L/mg)	-0.0083	
	R	0.999	
Langmuir 3	q_m(mg/g)	-15.208	y =119.75-15.208
	K_a (L/mg)	-0.0083	
	R	0.999	
Langmuir 4	q_m(mg/g)	-15.301	y = 0.0083+0.127
	K_a (L/mg)	-0.0083	
	R	0.999	

Table 3: The Parameters Obtained From The Isotherm Models For Ivermectin Biosorption (1.0 g)

Isotherm	Parameters	Values	Equations
Freundlich	N	0.447	y = 2.2344x-2.8157
	K_f(mg/g)(L/mg)$^{1/n}$	0.0015	
	R	0.898	
Langmuir 1	q_m(mg/g)	-6.0679	y =-0.1648x+20.794
	K_a (L/mg)	0.0480	
	R	0.5848	
Langmuir 2	q_m(mg/g)	-2.328	y =34.804-0.4294
	K_a (L/mg)	-0.0123	

	R	0.850	
Langmuir 3	q_m (mg/g)	-7.9419	y =110.17x-7.9419
	K_a (L/mg)	-0.009	
	R	0.775	
Langmuir 4	q_m (mg/g)	-30.236	y =0.0055x+0.1663
	K_a (L/mg)	-0.0055	
	R	0.775	

It is well known that Gibbs free energy would define system non spontaneity. Gibbs free energy (ΔG) can be calculated from the following equlations:

$$K_c = C_a / C_e$$
$$\Delta G = -RT \ln K^0_{\epsilon}$$

where K_c is the equilibrium constant, K^0_{ϵ} is the thermodynamic equilibrium constant C_a is the equilibrium concentration in solution (mg/L) R is the universal gas constant 8.314 J/mol, and T is temperature (K). Thermodynamic equilibrium constant (K^0_{ϵ}) can be calculated from the equilibrium constant by plotting equilibrium constant against initial ivermectin concentration [12].

Table 4: Comparison of gibbs free energy values for various system

Sorbent	Drug	ΔG (kj/mol)	T (K)
Aktivated Sludge (0.5 g) (This work)	Ivermectin	0.997	298
Activated Sludge (1.0 g) (This work)	Ivermectin	4.720	298
Kaolin (0.25 g)[1]	Metmorfin HCl	3.43	310.50
Attapuligate (0.25 g)[1]	Metmorfin HCl	1.017	310.50

Table 4 shows the comparision of Gibbs free energy values adsorbents. The positive ΔG values confirm the nonspontaneous nature of adsorption process, there is some sort of interactions but weak interactions.

4. Discussion

From the work presented here following conclusions can be drawn;

- Ivermectin was adsorbed by live activated sludge to some degree,
- Biosorption was fast completed with in 20 minutes.
- The positive ΔG values confirm the nonspontaneous nature of adsorption process.

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