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Dubinin–radushkevich isotherm studies of equilibrium biosorption of some veterinary pharmaceuticals by using live activated sludge

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Abstract

Environmental protection has increased over the years all over the world. In this investigation, the adsorption properties of live activated sludge (0.5 g and 1 g) for ivermectin, metamizol sodium and gentamicin sulfate were performed as a biosorbent. The biosorption of these veterinary pharmaceuticals were investigated in a batch system. The equilibrium adsorption data were described by Dubinin-Radushkevich (D-R) adsorption isotherm model. The adsorption equilibrium is attained within 20 min for ivermectin and gentamicin sulfate and 10 min for metamizol sodium. The estimated values of adsorption energy, Ea, calculated from the D-R isotherm, for all pharmaceuticals, ivermectin and live activated sludge (1.0 g) system were found to be 9,622 kJ mol^{-1} at room temperature, which implies that adsorption of ivermectin onto live activated sludge (1.0 g) is by ion exchange.

Keywords: Biosorption; dubinin-radushkevich; isotherm; drug.

1. Introductıon

Since the 1990s, pharmaceutical substances have been detected in surface water. Ternes (1998); Halling-Sørensen *et al.* (1998); Heberer (2002); Dordio *et al.* (2009) recognized pharmaceuticals as new unregulated contaminants (Ternes, 1998; Halling-SØrensen, *et al.* 1998; Heberer, 2002; Dordio *et al*., 2009). However, most of the previous study focused on human pharmaceuticals. Veterinary drugs are receiving very little attention. Nonetheless, they are being detected in aquatic environment in the USA, Europe and Asia (Carvalho *et al*., 2013). Veterinary pharmaceuticals are released to the environment through various pathways; their environmental presence may disturb ecological balance and lead to unforeseen effects on humans and animals (Matsuia *et al*., 2008). Many of these compounds are hardly biodegradable for which, much is yet unknown on their fate and potential impact on environment. Several studies have reported that adsorption is an important pathway accounting for drug removal from the water phase in activated sludge process (Kim *et al.*, 2005).

Metamizol sodium is a non-steroidal anti-inflammatory drug. Ivermectin is derived from a naturally-occurring fermentation product and, is an important antiparasitic agent. It consists of 2 homologues: not less than 80% 22,23-dihydroavermectin B_{1a} (H_2B_{1a}) and not more than 20% 22,23-dihyroavermectin B_{1b}(H_2B_{1b}). It is a widely used anti-parasitic drug (Li *et al.*, 1997). Antibiotics have wide range of uses in both human and veterinary medicine. In the livestock industry, the use of antibiotics as growth promoters as well as therapeutic agents is very common (Bekçi *et al*., 2006). Gentamicin is an aminoglycoside antibiotic with a wide spectrum of antibacterial activity for humans. Gentamicin sulfate is an aminoglycosidic antibiotic for bacterial infections caused by staphylococcus, which are sensitive to Gram-positive bacteria in animals (Haghbın-Nazarpak *et al*., 2010).

Adsorption may be one of the methods for the removal of dyes, heavy metals and pharmaceuticals from waste water. However, it is an extremely important process, because it may effect the fate and impact of chemicals in the environment. The adsorption of pollutants from solution plays an important role in waste water treatment. This process involves various interactions such as hydrophobic, electrostatic attraction and hydrogen bonding (Gunay *et al*., 2007; Altin *et al*., 1998; Qadeer, 2007; Barkakatia *et al*., 2010).

Dubinin-Radushkevich equation is one of the most popular isotherm equations in adsorption theory. It is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The model has been often successfully fitted

with high solute activities and the intermediate range of concentrations data. However, it has unsatisfactory asymptotic properties and does not predict the Henry's law at low pressure (Dabrowski, 2001; Gil & Grange, 1996).

In this study, adsorption of three commonly used veterinary pharmaceuticals (ivermectin, metamizol sodium and gentamicin sulfate) in batch system is investigated. The results of the equilibrium experiments have been applied to Dubinin-Radushkevich (D-R) adsorption isotherm model.

2. Experimental

2.1. Preparation of biosorbent

Activated sludge was collected from full scale activated sludge plant of Pepsi Soft Drink Filling Industry, Adana, Turkey. The biosorbent was used on the same day of collection. Total suspended solids were measured by the standard gravimetric technique (Standard Methods, 1998).

2.2. Preparation of pharmaceutical solutions for biosorption

Test solutions containing pharmaceuticals were prepared by fresh stock pharmaceuticals solution, which was obtained by dissolving weighed quantity of ivermectin, gentamicin sulfate and metamizol sodium in methanol and distilled water.

2.3. Batch studies

The sorption tests were conducted in a routine manner by a batch technique at 25 ºC. The data for deriving the isotherms constant were obtained by using sludge (0.5 g and 1.0 g) and pharmaceutical 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 pharmaceuticals. All the experiments were carried out in duplicate.

2.4. Analysis of the concentration of pharmaceuticals

The final concentration of pharmaceuticals in solution was measured using an UV-VIS spectrophotometer (Perkin Elmer) at a wavelength of 255 nm for gentamicin sulfate, 245 nm for ivermectin and 253 nm for metamizol sodium. The amount of pharmaceuticals, biosorbent onto activated sludge biosorbent, qe (mg g^{-1}), was calculated by a mass balance relationship as follows:

$qe = (C0-Ce)\ V/W$

where, C0 and Ce are the initial and equilibrium liquid-phase concentration of pharmaceuticals, respectively (mg L^{-1}), V the volume of the solution (L) and W is the dry weight (g) of activated sludge.

Dubinin-Radushkevic isotherm is an empirical model initially conceived for the adsorption of subcritical vapors onto micropore solids following a pore filling mechanism. The approach was usually applied to distinguish the physical and chemical adsorption of metal ions, with its mean free energy, E per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity) can be computed by the relationship (Dubinin, 1960; Hopson, 1969; Gupta *et al*., 2009).

$$E = \left[\frac{1}{\sqrt{2B_{DR}}}\right]$$

Where B_{DR} is denoted as the isotherm constant. Meanwhile, the parameter ε can be correlated as:

$$\varepsilon = RTln\left[1 + \frac{1}{C_e}\right]$$

Where R, T and C_e represent the gas constant (8.314 J/mol K), absolute temperature (K) and adsorbate equilibrium concentration (mg/L) respectively. One of the unique features of the Dubinin-Radushkevich isotherm model lies on the fact that it is temperature-dependent, which when adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed vs. the square of potential energy, all suitable data will lie on the same curve, name as the characteristic curve (Foo *et al*., 2010; Dada *et al*., 2012).

3. Results and discussion

In order to investigate the mode of adsorption of veterinary pharmaceuticals onto live activated sludge (whether it is physical or chemical in nature), the equilibrium data 298 K was applied to the D-R isotherm model. Dubinin-Radushkevich Isotherm Model constants and correlation coefficients for adsorption Of Ivermectin, Gentavilin and Metamizol Sodium are shown in Table 1. It is known that magnitude of apparent energy E is useful for estimating the type of adsorption and if this value is below 8 kJ/mol the adsorption type can be explained by physical adsorption. If it is between 8 and 16 kJ/mol the adsorption type can be ion exchange and at values over 16 kJ/mol, the adsorption type can be explaned by a stronger chemical adsorption than ion exchange (Mobasherpour *et al*.,2012; Chowdhury *et al*., 2011).

Table 1. Dubinin-radushkevich Isotherm model constants and correlation coefficients for adsorption of ıvermectin, gentavilin and metamizol sodium

D-R Isotherm Model	Ivermectin (0.5 g adsorban)	Gentamicin sulfate (0.5 g adsorban)	Metamizol Sodium (0.5 g adsorban)
B	5E-0.5	1E-0.5	5E-0.6
E (kJ/mol)	-	-	-
R^2	0.1807	0.308	0.7028
D-R Isotherm Model	Ivermectin (1.0 g adsorban)	Gentavilin (1.0 g adsorban)	Metamizol Sodium (1.0 g adsorban)
B	0.0054	8E-0.6	2E-0.5
E (kJ/mol)	9.622	-	-
R^2	0.7708	0.4296	0.2845

D-R model was used to estimate the porosity apparent free energy and the characteristic of adsorption (Dubinin & Radushkevich, 1974). The estimated values of E for the present study were found to be >8 kJ/mol, which implies that adsorption of ivermectin onto activated sludge (0.5 g) is by ion exchange. Similar results were found by Domínguez *et al,* for Trimethoprim- XAD-7 resin systems (E=10.10 kJ/mol), Carbamazepine - XAD-7 resin systems (E=8.84 kJ/mol), Ketoprofen-- XAD-7 resin systems (E=9.45 kJ/mol) and Naproxen-- XAD-7 resin systems (E=8.28 kJ/mol) (Dominguez *et al*., 2011).

The lower value of R^2 for gentamicin sulfate and metamizol sodium of D-R model indicate not usefulness of this model to fit the experimental data. Similar results were reported by Bucur *et al.* (2011) for cesium-geologic formations systems. The lower value of R^2 (0.42) for cesium-clay systems of D-R model does not indicate to fit with the experimental data (Bucur *et al*., 2011).

The plot of In qeq versus ε^2 is displayed in Figure 1-2-3 for ivermectin, metamizol sodium and gentamicin sulfate and activated sludge systems.

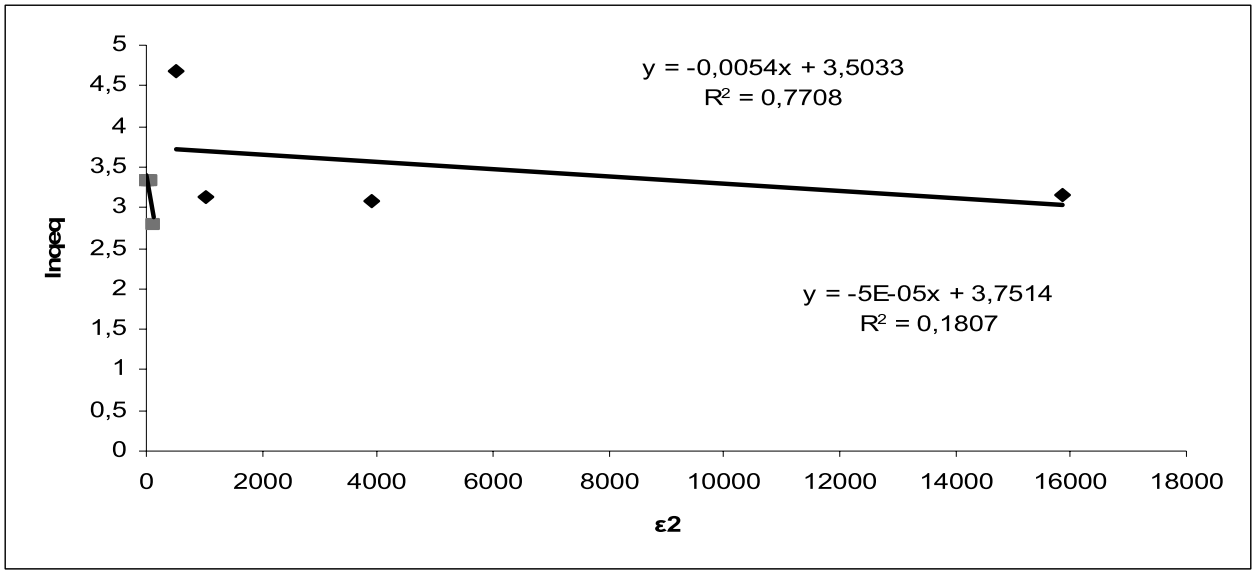

Fig. 1. Dubinin-Radushkevich Isotherm for vermectin

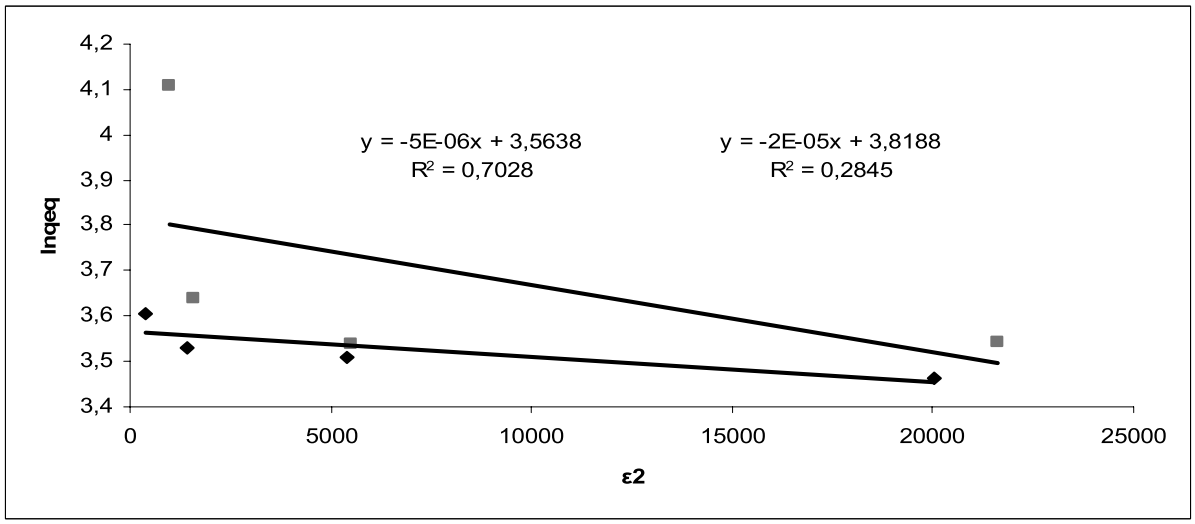

Fig. 2. Dubinin-radushkevich ısotherm for metamizol sodium

The obtained coefficients of determination (R^2) for the Dubinin-Radushkevich model does not indicate usefulness of this model to fit with the experimental data for ivermectin-activated sludge system (1.0 g), metamizol sodium-activated systems (0.5-1.0 g) and gentamicin sulfate-activated sludge systems (0.5-1.0 g). Similar results were also reported by Fakhri and Behrouz for MgO nanoparticles and ZnO-MgO nanocomposite-linezolid antibiotic systems (Fakhri and Behrouz, 2015). They found β values are 5E-9 and 6E-3 for Mg nanoparticles-antibiotic systems, ZnO-MgO-antibiotic systems respectively. Second similar results reported by Sunettha *et al.* (2015) for floride-activated carbon that it is derived from Abutilon indicum plant. They found the slope of -5E-08 (Fakhri & Behrouz, 2015).

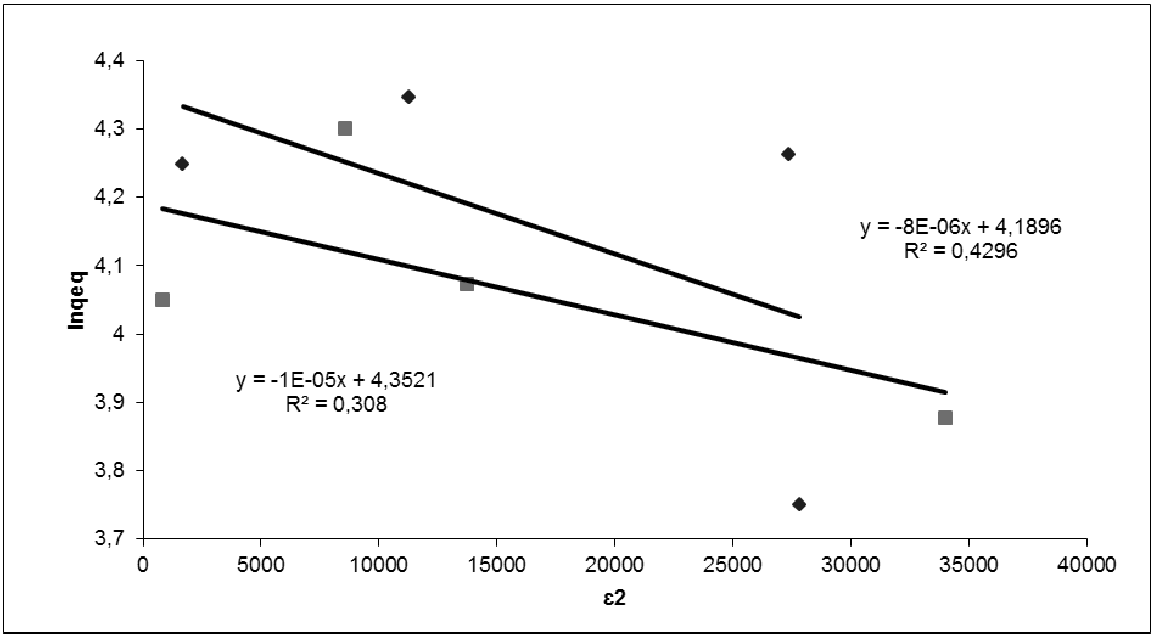

Fig. 3. Dubinin-radushkevich ısotherm for gentamicin sulfate

4. Conclusion

In this paper, investigation of the equilibrium sorption was carried out at room temperature for 160 min with three different veterinary pharmaceuticals and activated sludge (0.5 g-1 g) as adsorbent. Dubinin-Radushkevich Isotherm model was studied. The adsorption data was fitted into Dubinin-Radushkevich Isotherm for ivermectin onto live activated sludge (1.0 g). The ivermectin-activated sludge system (0.5 g) was found to be have the best fit.

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دراسات دوبينين ردايشكوفيش الأيزوترمية الخاصة بتوازن الأمتصاص لبعض المواد الدوائية البيطرية بإستخدام الحمأة المنشطة

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الملخص

لقد ازداد الإهتمام بحماية البيئة على مر السنين وعلى مستوى العالم. في هذه الدراسة نتحقق من خصائص الإمتزاز للحمأة المنشطة (1 – 0.5 غرام) الخاصة بالصادات الحيوية (الإيفرميكتين، ميتاميزول الصوديوم، جينتاميسين السلفات) كماصات حيوية. لقد تم التحقق من الإمتصاص الحيوي لهذه المواد الدوائية البيطرية باستخدام نظام الدفعة. إن المعطيات الخاصة بتوازن الإمتزاز تم وصفها بإستخدام معادلة دوبينين – راديشكوفيش (D-R). إن توازن الإمتزاز الخاص بالإيفرميكتين و جينتاميسين السلفات تم بلوغه بعد 20 دقيقة أما توازن الإمتزاز الخاص بميتاميزول الصوديوم فتم بلوغه بعد 10 دقائق.

إن القيم التقديرية لطاقة الإمتزاز تم حسابها من معادلة دوبينين – راديشكوفيش (D-R) لكل المواد الدوائية، فطاقة الإمتزاز للحمأة المنشطة الخاصة بالإيفرميكتين كانت (9.622 كيلو جول/ مول) عند درجة حرارة الغرفة ممايعني أنه تبادل أيوني.

كلمات دالة: امتصاص حيوي، إيزوترم، دوبينين – راديشكوفيش، دواء.