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Modeling of adsorption isotherms of pharmaceutical products onto various adsorbents: A Short Review

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Abstract

The frequent contamination of water resources with pharmaceutical products has been attracted enormous environmental researchers. Because those pharmaceutical compounds are commonly detected in wastewater, sewage, surface water, groundwater and even drinking water. This paper presents a short review of adsorption isotherms of pharmaceutical products from aqueous solution by various adsorbents such as activated carbons, clays and agricultural solid wastes. Several isotherm models such as Langmuir, Freundlich, Temkin, Dubinin– Radushkevich, Sips, Toth and Redlich-Peterson are described. The present short review reveals that the equilibrium data fitted Langmuir isotherm in majority of cases and has successful application in many sorption processes of monolayer adsorption. Most of the reported studies are performed in the batch process; this gives a platform for the designing of the continuous flow systems with industrial applications at the commercial level also.

1. Introduction

Emerging contaminants (ECs) are those compounds found in wastewater in low concentrations as a consequence of the new habits of consume developed in our society. The discharge limitations of these compounds are not completely or not at all regulated, which can result in real hazards to the human health and environment [1, 2]. Among the compounds considered as ECs includes many different substances such as, pharmaceutical and personal care products, food additives, plasticizers, pesticides, etc. [3]. Pharmaceuticals are a group of chemical compounds substances that have medicinal properties, and unfortunately represent a significant category of microcontaminants emerging in aqueous environments from point and diffuse sources.

Pharmaceuticals detected in surface waters are antibiotics, anticonvulsants, painkillers, cytostatic drugs, hormones, lipid regulators, b-blockers, antihistamines, and the diagnostic X-ray contrast medium amidotrizoic acid, whose concentrations range from ng L^{-1} to mg L^{-1} in wastewater treatment plant effluents and surface waters [4]. Their low concentration makes their detection and elimination in conventional water treatment plants very difficult [5]. The several possible sources and routes for the occurrence of pharmaceuticals in aquatic environments are summarized in Figure 1 [6].

During a treatment period, the pharmaceuticals are excreted from patient's body either unchanged or in the form of derivatives or metabolites and are incorporated in wastewaters [7]. The presence of pharmaceuticals in the environment can lead to disruption of physiological processes and the reproductive function of living organisms. Note that the development of antibiotic-resistant bacteria strains could cause that the drug metabolites can act as catalysts for undesirable environmental processes [8]. The development of antibiotic resistance has led to a reduction in the number of effective antibiotics available to treat human's infectious diseases and, consequently, the World Health Organization (WHO) has identified the antibiotic resistance as a global threat to humanity [9]. Therefore, it is important to take action against the pharmaceutical products pollution of the environment [10; 11].

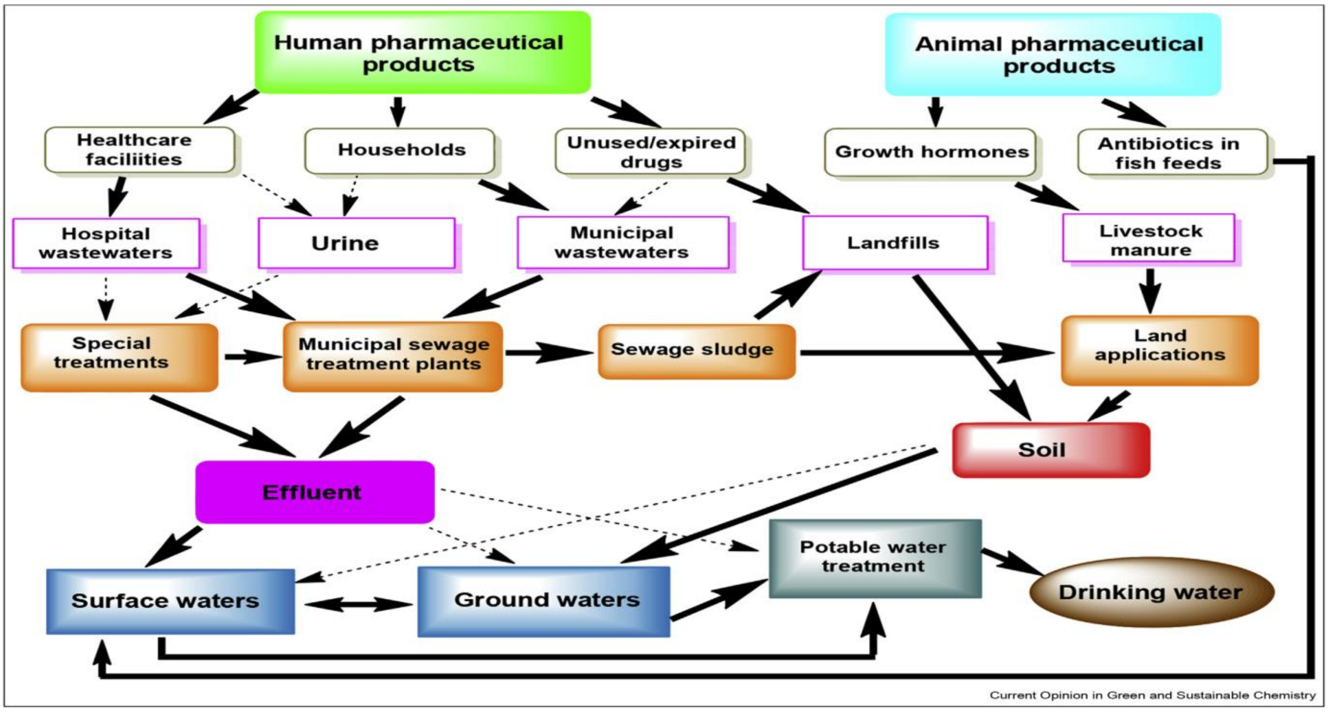

Figure 1: Potential routes for human and animal pharmaceutical products to contaminate aquatic environment [6]

Several methods have been applied for treatment of pharmaceutical products like photocatalytic degradation [12-19], micro extraction [20-24], oxidation [25-28], biodegradation [29-32], chlorination [33- 37], biofiltration [38-40], nanofiltration and reverse osmosis [41-43], electrochemical oxidation [44-47], and adsorption [48-60]. Adsorption is a well-known equilibrium separation process and an effective method for water decontamination applications [61-68]. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances.

The aim of this short review paper was to describe the modeling of adsorption isotherms of pharmaceutical products from aqueous solutions by various adsorbents. The objective is not an exhaustive review of all the types of adsorbents used, but to focus onto activated carbons, clays and agricultural solid wastes. The reader is strongly encouraged to refer to the original research papers for information on experimental conditions and others.

2. Modeling of adsorption isotherms

Adsorption isotherms describe the relationship between the equilibrium concentration of the adsorbed matter in the solution and the amount of adsorbed matter on the surface of the adsorbent. Adsorption equilibrium is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration [69]. Several isotherm models such as Langmuir, Freundlich, Temkin, Dubinin–Radushkevich, Sips, Toth and Redlich-Peterson are described in this present short review article:

Langmuir isotherm. Langmuir isotherm model assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface [70].

Freundlich isotherm. Freundlich isotherm is applicable to adsorption processes that occur on heterogonous surfaces. This isotherm gives an expression which defines the surface heterogeneity and the exponential distribution of active sites and their energies [70].

Temkin Isotherm. Temkin isotherm model takes into account the effects of indirect adsorbate/adsorbate interactions on the adsorption process; it is also assumed that the heat of adsorption (ΔHads) of all molecules in the layer decreases linearly as a result of increase surface coverage. The Temkin isotherm is valid only for an intermediate range of ion concentrations [71].

Dubinin-Radushkevich isotherm. Dubinin-Radushkevich model is the fact that it is temperature dependent; hence when adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed versus the square of potential energy [72].

Sips isotherm. Sips isotherm is a combination of the Langmuir and Freundlich isotherms**.** This model is suitable for predicting adsorption on heterogeneous surfaces, thereby avoiding the limitation of increased adsorbate concentration normally associated with the Freundlich model. Therefore at low adsorbate concentration this model reduces to the Freundlich model, but at high concentration of adsorbate, it predicts the Langmuir model [73].

Toth isotherm. Toth isotherm model combines the characteristics of both the Langmuir and Freundlich isotherm. It approaches the Freundlich model at high concentration and is in agreement with the low concentration limit of the Langmuir equation model [74].

Redlich–Peterson isotherm. Redlich–Peterson isotherm model combines elements from both the Langmuir and Freundlich equation model and the mechanism of adsorption is a hybrid one and does not follow ideal monolayer adsorption. It is used as a compromise to improve the fit by Langmuir or Freundlich equation model [74].

3. Removal of pharmaceutical products by activated carbons

Efforts have been made by many scientists to propose alternative carbon source for producing activated carbons at lower costs. Activated carbons are generally manufactured by pyrolysis of biomass [75], under inert atmosphere. The activation may be chemical or physical.

Çalışkan & Göktürk [76] studied the removal of sulfamethoxazole and metronidazole onto activated carbon from aqueous solutions. Adsorption isotherms have been modeled by Freundlich, Langmuir, and Dubinin- Raduskevitch models. The adsorption of these drugs was better represented by the Langmuir model. Maximum adsorption capacities of sulfamethoxazole and metronidazole were found to be 185.19 and 144.93 mg g^{-1} respectively. Baccar *et al.* [77] investigated the adsorption of naproxen, diclofenac, ibuprofen, and ketoprofen on activated carbon prepared from olive-waste cakes. The results showed that the Langmuir model provided the best fit with a monolayer adsorption for the four considered pharmaceuticals. Maximum adsorption capacities of Naproxen Ketoprofen, Diclofenac and ibuprofen were found to be 39.5, 24.7, 56.2 and 12.6 mg g^{-1} respectively. Ferreira *et al.* [78] studied the adsorption of paracetamol using activated carbon of Dende and Babassu Coconut Mesocarp. Equilibrium data may be represented by Langmuir model with the monolayer adsorption capacities were found to be 70.62 and 71.39 mg g^{-1} at activated carbon originated from dende coconut mesocarp and babassu coconut mesocarp, respectively. Mukoko *et al.* [79] studied the adsorption of aspirin, paracetamol and ibuprofen from hospital effluent using activated carbon prepared from rice hull. The Langmuir model showed best fit for ibuprofen and paracetamol adsorption onto activated carbon. The Freundlich model showed best fit for aspirin adsorption onto activated carbon. Maximum adsorption capacities of aspirin, paracetamol and ibuprofen were found to be 178.89, 169.49 and 100 mg g^{-1} respectively. Miao *et al.* [80] studied the adsorption of cephalexin from effluent by activated carbons produced from alligator weed by phosphoric acid activation. The Langmuir isotherm gave the best fitted with the experimental data at 308 K and the monolayer adsorption capacities were found to be 38, 40 and 45 mg g^{-1} at 288, 298 and 308 K, respectively. Marzbali *et al.* [81] studied Tetracycline batch adsorption in a synthesized aqueous solution using activated carbon prepared from apricot shell. Adsorption isotherms were investigated, and it was shown that the Freundlich model was the best fit for the adsorption equilibrium data. The maximum adsorption capacity of Tetracycline onto activated carbon was 308.33 mg g^{-1}. Nazari *et al.* [82] investigated the batch adsorption experiments for the adsorption of cephalexin antibiotic on walnut shell activated carbon prepared by chemical activation in the presence of $ZnCl_2$. The adsorption isotherm was analyzed by different isotherm models. It was found that the Freundlich and Toth models provided the best fit for the experimental data. The maximum adsorption capacity was obtained 233.1 mg g^{-1} based on the Langmuir model. Boudrahem *et al.* [83] investigated the feasibility of the preparation of activated carbon cloths from waste textiles for the removal of clofibric acid, tetracycline and paracetamol. The equilibrium data for the adsorption of pharmaceuticals compounds onto activated carbon cloths were analyzed by testing different models. The results showed that the Langmuir model provided a good description of the experimental isotherms for tetracycline and paracetamol, whereas clofibric acid isotherm rather follows the Freundlich model. On the basis of the Langmuir analysis, the maximum adsorption capacities were determined to be 109 and 105 mg g^{-1} for tetracycline and paracetamol, respectively. Beltrane *et al.* [84] prepared activated carbon fibers from pineapple plant leaves which was used the adsorption of caffeine onto its surface. It was found that the Langmuir isotherm models were best fitted to the experimental data and the monolayer adsorption capacity was found to be 155.50 mg g^{-1}. Wong *et al.* [85] reported conversion of spent tea leaves to activated carbon for removal of acetaminophen (paracetamol) from simulated wastewater. The adsorption data were well fitted to the Langmuir isotherm model. The adsorption capacity of activated carbon derived spent tea leaves towards acetaminophen was found to be 59.2 mg g^{-1}. Paredes- Laverde *et al.* [86] prepared activated carbons from rice husk and coffee husk for the removal of acetaminophen in both distilled water and synthetic urine. The adsorption process showed a well-fit to the Redlich-Peterson isotherm. β values of approximately 1, indicated that the process resembles Langmuir, and suggests a homogeneous adsorption process. These results presented above showed that the excellent ability and economic promise of the activated carbons prepared from biomass exhibited high sorption properties.

4. Removal of pharmaceutical products by clays

Clays are abundantly available and hence low cost [87]. Well-known classes of clays include illite, serpentine, diatomite, montmorillonite, saponite, bentonite, kaolinite, pylophyllite, Fuller's earth, sepiolite and vermiculite [88]. A relatively good removal capability of clays to uptake pharmaceutical products has bee demonstrated by many researchers. Montmorillonite KSF was used by Bekci *et al.* [89] for removal of trimethoprin under different conditions (pH, ionic strength, temperature). The adsorption data could be fitted with Freundlich, Langmuir and Dubinin-Radushkevich equation models to find the characteristic parameters of each model. It was found that linear form of Langmuir isotherm seems to produce a better model than linear form of Freundlich equation model. From the Langmuir and Freundlich models, the adsorption capacity values raised as the solution temperature decreased. From Dubinin–Radushkevich isotherm, it was also determined that the type of adsorption can be considered as ion-exchange mechanism. Bekci *et al.* [90] studied the adsorption of trimethoprim onto K10 montmorillonite using batch technique under different pH and temperature. The adsorption of trimethoprim has been described by using Langmuir, Freundlich and Dubinin–Radushkevich equation models to obtain adsorption capacity values. The results indicated that the relative adsorption capacity values (K_F) are decreasing with the increase of temperature in the range of 298– 318 K. The adsorption energy values obtained from Dubinin–Radushkevich isotherm showed that adsorption of trimethoprim onto K10 can be explained by ion exchange mechanism at 298, 308 and 318 K. Fukahori *et al.* [91] studied the adsorptive removal of five sulfa drugs (sulfathiazole, sulfamerazine, sulfamethizole, sulfadimidine and sulfamethoxazole) from an aqueous solution using a high-silica zeolite. Langmuir and Freundlich models were applied to the experimental data obtained under various pH conditions. The experimental data fit better to the Langmuir model compared to the Freundlich model, thus a pH-dependent adsorption model based on the Langmuir isotherm. Thiebault *et al.* [92] studied the adsorption of tramadol and doxepin on sodium exchanged smectite. The adsorption isotherms for both temperatures of 20 and 40 °C and the derived data determined through the fitting procedure by using Langmuir, Freundlich and Dubinin– Radushkevich equation models explicitly pointed out that the adsorption of both tramadol and doxepin is mainly driven by electrostatic interaction. Sharipova *et al.* [93] studied the adsorption of model systems of triclosan by mineral sorbent diatomite. Adsorption isotherms were analyzed according to the linear/nonlinear form of Langmuir, Freundlich, Sips and Toth isotherm models. The results showed that nonlinear Langmuir and Sips isotherm models provided suitable fitting results and no pronounced difference in adsorption efficiency between isotherms measured after 1, 2 and 3 days adsorption was observed. Maximum adsorption capacity of diatomite towards triclosan q_s is 140 mg g^{-1}. Fuad *et al.* [94] reported on the removal of ibuprofen, diclofenac sodium, indomethacin, chlorpheniramine maleate, and paracetamol from water using the natural Jordanian zeolite as an adsorbent. Langmuir and Freundlich isotherm models were used to evaluate the adsorption efficiencies of the investigated pharmaceuticals. The results showed that Langmuir isotherm fits the experimental data for diclofenac sodium, indomethacin and paracetamol with adsorption capacity of 4.8, 26.6 and 55.6 mg g^{-1}, respectively, whereas Freundlich isotherm fits the experimental data for both ibuprofen and chlorpheniramine maleate. Del Mar Orta *et al.* [95] studied the potential use of the smectite clay mineral montmorillonite as adsorbent in the removal of water containing the propranolol. Propranolol adsorption onto Montmorillonite was well described by the Freundlich and Dubinin- Radushkevitch models, being the ionic exchange between charged propranolol and inorganic cations in the free sites the most favorable pathway. Additionally, the variable pH presented a low influence in the range of 1 to 9. The results presented above show that clay materials may be promising adsorbents from environmental and purification point of views.

5. Removal of pharmaceutical products by agricultural solid wastes

Agricultural waste materials have little or no economic value and often pose a disposal problem [96]. The raw agricultural solid wastes such as leaves, seeds etc. and waste materials from forest residues have been used as adsorbents. These materials are available in large quantities and may be potential adsorbents due to their physico-chemical characteristics and low cost [97].

The work of Araujo *et al.* [98] described the removal of Diclofenac in batch experiments from an aqueous environment using adsorption onto *Moringa Oleifera* seed husk biomass. The adsorption equilibrium data better fit the Freundlich model. Paredes-Laverde *et al.* [99] studied the removal of the widely used antibiotic norfloxacin using rice and coffee husk wastes as adsorbents. The equilibrium adsorption data were analyzed using Langmuir, Freundlich and Redlich-Peterson isotherms. The best fit for the Langmuir and Redlich-Peterson isotherms suggested a monolayer-type adsorption model. N'diaye and Kankou [100] used *Balanites aegyptiaca* seeds as a low cost adsorbent for adsorption of caffeine from aqueous solution. Batch sorption experiments are intended to identify the adsorption isotherms of the caffeine on the *Balanites aegyptiaca* seeds. Four isotherm models (Freundlich, Langmuir, Redlich–Peterson and Sips) were tested for modeling the adsorption isotherms by nonlinear method. The maximum adsorption capacity was found to be 4.28 mg g^{-1}. *A Zizyphus mauritiana* seed as adsorbent was investigated by N'diaye and Kankou [101] for the removal of caffeine from aqueous solution. Equilibrium isotherms were determined and analyzed by nonlinear method using the Langmuir, Freundlich, Temkin, Sips, Redlich – Peterson and Toth isotherms. The results showed that the Langmuir isotherm model were best fitted to experimental data and the monolayer maximum adsorption capacity was found to be 2.38 mg g^{-1}. N'diaye *et al.* [102] studied the adsorption of paracetamol on groundnut shell as low cost adsorbent using the batch equilibrium method. The experimental data were fitted to the Langmuir, Freundlich, Temkin, Sips, Redlich – Peterson and Toth. The Langmuir better described the isotherm data. The retention of paracetamol on the groundnut shell showed a relatively significant adsorption with a maximal quantity of 3.02 mg g^{-1}. The results presented above showed the potential application of agricultural wastes as low-cost alternative for the removal of pharmaceutical products which are in good agreement and widely discussed in literature [103-105].

Conclusion

This short review is devoted to the adsorption of pharmaceutical products from aqueous solutions, which are chemical compounds that have been detected in the aquatic environment and belong to some of the most popular emerging pollutants that may cause serious environmental and human health problems. The modelings of adsorption isotherms of pharmaceutical products from aqueous solutions by various adsorbents have been reviewed. There are some conclusions from this short review as following:

- The current short review highlights the enormous potential of biomass waste to be used as low cost adsorbent or as precursors for the synthesis of activated carbons for the adsorption of pharmaceutical products.
- Literature also reveals that the equilibrium data fitted Langmuir isotherm in majority of cases and in few cases for Freundlich isotherm.

Most of the reported studies are performed in the batch process; this gives a platform for the designing of the continuous flow systems with industrial applications at the commercial level also.

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