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Removal of atrazine by adsorption onto Various adsorbents: A Short Review

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Abstract

Adsorption techniques are widely used to remove certain classes of pesticides such as organochlorines, organophosphates, carbamates, pyrethroids, organonitrogenates, triazines and benzimidazoles from waters. In this short review paper, we describe the adsorption of atrazine from aqueous systems onto various adsorbents and some variables governing the efficiency of the process. The atrazine removal process followed Langmuir model and pseudo-second order kinetic in majority of the cases. The adsorption of atrazine is found to be a spontaneous process ($\Delta G < 0$) and this process may be endothermic or exothermic. The adsorption process parameters had an important role on the removal efficiency of atrazine from aqueous solution. Further more interest should be concentrated by the researchers to predict the performance of the adsorption process for atrazine removal from real waters. In addition, 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.

1. Introduction

Emergent pollutants are defined as chemical compounds present in the environment, such as pesticides, pharmaceuticals, food packaging, hygiene products and industrial additives [1]. They find way into the environment via several pathways and the same is diagrammatically shown in Figure 1 [2].
Among the emergent pollutants there are pesticides. According to the target organism, pesticides are classified as insecticides, fungicides, herbicides, and acaricides, among others, with herbicides representing around 50 % of all pesticides used in agriculture [3].
Atrazine (1-chloro-3-ethylamino-5-isopropylamino-2, 4, 6-triazine) (Figure 2) is one of the most widely herbicide used since the 1950s [4]. Although atrazine is banned in Europe [5], it is still widely used in Africa and United States [6-8].
Atrazine is used to prevent pre- and post- emergence of broadleaf weeds and grassy weeds in crops such as guava, sorghum, pineapple, sugarcane, maize, lupins, nut orchards, residential lawns summer fallow, and eucalypt plantations [9].
Consequently, atrazine is frequently detected in groundwater [10-14], surface water [15-18] and soils [19; 20] due to its high leaching potential and high chemical stability. The basic physicochemical properties of atrazine are given in Table 1.

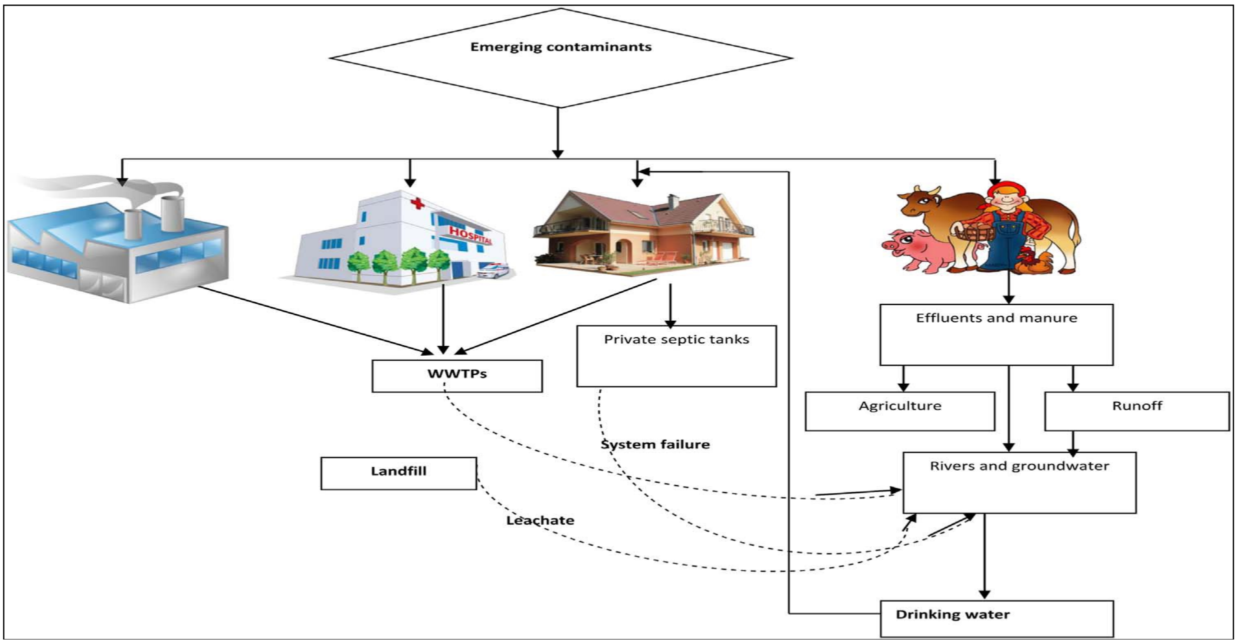

Figure 1. *Sources of emerging contaminants into the environment [2]*

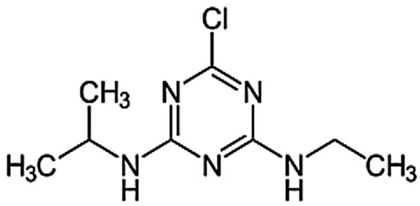

Figure 2. *Atrazine chemical structure*

Table 1: Physicochemical characteristics of atrazine

Molecular formula	$C_8H_{14}ClN_5$
Molar mass (g mol^{-1})	215.7
Water solubility at 20°C (mg L^{-1})	30
pKa	1.64
Log K_{ow}	2.75
Density	1.187 at 20 °C

Several researchers have used different techniques to remove atrazine and other pesticides from aqueous solutions. These include the photo Fenton treatment [21-24], aerobic degradation [25-27], photocatalytic degradation [28-32], electro dialysis membranes [33; 34], ozonation [35-39] and adsorption [40-62]. However, adsorption is one of the most widely applied techniques for pollutant removal. Adsorption has been found to be superior to other techniques in terms of flexibility and simplicity of design, initial cost, insensitivity to toxic pollutants and ease of operation. Adsorption also does not produce the harmful substances [63].

In this short review article, we report on adsorption of atrazine onto various adsorbents as well as the influences of various adsorption process variables i.e. solution pH, adsorbent dosage, temperature and initial atrazine concentration on the removal efficiency of atrazine from aqueous solutions.

2. Adsorption

The term adsorption refers to the accumulation of a substance at the interface between two phases (liquid-solid interface). The substance that accumulates at the interface is called adsorbate and the solid on which adsorption occurs is adsorbent [64].

Adsorption can be classified into two types: chemical adsorption and physical adsorption. Chemical adsorption or chemisorption is illustrated by the formation of strong chemical associations between molecules or ions of adsorbate to adsorbent surface [65] and thus chemical adsorption generally is irreversible. Physical adsorption or physisorption is characterized by weak Van der Waals intraparticle bonds between adsorbate and adsorbent and thus reversible in most cases [65].

There are many factors affecting atrazine adsorption such as solution pH, temperature, initial atrazine concentration, etc. Thus, the effects of these parameters are to be taken into account. Optimization of such conditions will greatly help in the development of industrial-scale atrazine removal treatment process.

The adsorption uptake at equilibrium time q_e (mg g^{-1}), is expressed by following equation (1):

$$q_e = \frac{(C_i - C_e)V}{m} \qquad (1)$$

Where q_e is the atrazine concentration in adsorbent (mg g^{-1}), C_i is the initial atrazine concentration (mg L^{-1}); C_e is the atrazine concentration at equilibrium (mg L^{-1}); V is the solution volume (L) and m is the mass of the adsorbent used (g).

3. Adsorption isotherms and models

Adsorption equilibrium is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time [66]. A wide variety of equilibrium isotherm models such as Langmuir, Freundlich, Brunauer–Emmett–Teller, Redlich– Peterson, Dubinin– Radushkevich, Temkin, Toth, Koble–Corrigan, Sips, Khan, Hill, Flory–Huggins and Radke–Prausnitz isotherm, have been used [67]. However, Freundlich and Langmuir isotherms are the most commonly used isotherms by several researchers for different adsorbent/ adsorbate systems [68].

3.1 Langmuir adsorption isotherm model to atrazine adsorption

The Langmuir adsorption isotherm model assumed that adsorption takes place at specific homogeneous sites within the adsorbent, and it has been used successfully for many adsorption processes of monolayer adsorption [69]. The Langmuir equation is expressed by the following relation (2):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (2)$$

Where q_e is the amount of atrazine adsorbed per unit mass of adsorbent (mg g^{-1}), k_L is the Langmuir constant related to the adsorption capacity (L g^{-1}), C_e is the concentration of atrazine in the solution at equilibrium (mg L^{-1}), q_m is the maximum uptake per unit mass of adsorbent (mg g^{-1}).

3.2 Freundlich adsorption isotherm model to atrazine adsorption

The Freundlich adsorption isotherm model considers a heterogeneous adsorption surface that has unequal available sites with different energies of adsorption [70]. The Freundlich adsorption isotherm model is represented as follow (3):

$$q_e = K_F C_e^{1/n} \qquad (3)$$

Where K_F (mg g^{-1}) (L mg^{-1})^n and 1/n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

4. Atrazine adsorption Kinetic Study

Adsorption kinetics depends on the adsorbate–adsorbent interaction and system condition and has been investigated for their suitability for application in water pollution control. Two vital evaluation elements

for an adsorption process operation unit are the mechanism and the reaction rate [71]. Most of adsorption studies used pseudo-first-order and pseudo second- order models to study the adsorption kinetics [72]. Pseudo-first order equation of Lagergren, based on solid capacity with the assumption that the adsorption mechanism is rate limiting [73]. Pseudo-second order equation based on solid phase adsorption was also used with the assumption that the rate-limiting step may be chemical adsorption involving valence forces through sharing or exchange of electrons between the adsorbent and the adsorbate [74].
The nonlinear kinetics pseudo-first and pseudo-second order models may be expressed by equations (4) and (5), respectively:

$$q_t = q_e(1 - \exp^{-k_1 t}) \qquad (4)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \qquad (5)$$

Where q_t (mg g^{-1}) is the amount of atrazine adsorbed per unit mass of adsorbent at time t, q_e (mg g^{-1}) the amount of atrazine adsorbed at equilibrium, k_1 (L min^{-1}) is the pseudo-first order rate constant, k_2(gm $gmin^{-1}$) is the pseudo-second order rate constant and t is the contact time (min).

5. Removal of Atrazine

Some researchers explored the adsorption of atrazine from aqueous systems onto various adsorbents and some variables governing the efficiency of the process.
Among them, Chaparadza and Hossenlopp [75] studied the atrazine removal from water by treated banana peels. The effects of some variables governing the efficiency of the process such as pH, contact time, initial atrazine concentration, and temperature were investigated. Batch experiments showed that 15 g L^{-1} adsorbent dosage removed 90–99 % of atrazine from 1to 150 ppm aqueous solutions. The removal was both pH and temperature dependent with the most atrazine removed between pH 7 and 8.2 and increased with increasing temperature. The adsorption exhibited non-linear favorable adsorption behavior that could be well fitted by the Langmuir and Redlich–Peterson isotherm models. The maximum adsorption capacity was 14 mg g^{-1}. The Gibbs free energy and enthalpy were evaluated to be – 5.7 and 67.8 kJ mol^{-1}.
Bambara groundnut hulls powder as a biosorbent has been used by Sebata *et al.* [76] without any pretreatment for the removal of atrazine from aqueous solutions. The operating parameters investigated were pH, adsorbent dosage, contact time, initial concentration and temperature. The adsorption process was found to be highly pH dependent, with pH 7 being optimum. The biomass required at saturation was 0.9 g and the equilibrium was reached after 120 min. The Freundlich isotherm equation fitted the equilibrium data for atrazine adsorption. The equilibrium isotherm was reported to be pseudo- first order.
Wei *et al.* [77] used oil palm shell-based adsorbent for the removal atrazine from aqueous solution. Batch adsorption experiments were conducted to determine the effects of initial atrazine concentration (5 - 30 mg L^{-1}), contact time, adsorbent dosage (0.2 – 2 g) and solution pH (2 - 12) on the adsorption uptake of the adsorbent for atrazine. The adsorption uptake of atrazine increased with increasing initial concentration. The percentage of removal of atrazine increased with increasing adsorbent dosage, but it decreased as the solution pH increased. The equilibrium data were well described by the Freundlich isotherm model. Kinetic studies showed that the adsorption of atrazine on the oil palm shell-based adsorbent followed the pseudo-second order kinetic model.
Okeola *et al.* [78] prepared activated carbon by shell of *Thevetia peruviana* seed which was used to study the adsorption of atrazine onto its surface. Various parameters investigated showed that the adsorption of atrazine was found to be dependent on the initial concentration of atrazine, contact time, adsorbent dosage, pH and temperature of the medium. The adsorption data were analyzed according to the Langmuir, Freundlich and Temkin models which were found to be best fitted by the Freundlich isotherm. The pseudo- first order and the pseudo-second order models were tested in modeling the rate of the adsorption process. The adsorption process was found to obey pseudo second-order kinetics. The heat (ΔH^o), entropy (ΔS^o) and free energy (ΔG^o) of adsorption were determined to be -22.07, -0.24 and -0.68

kJ mol^{-1}, respectively. The negative values of ΔH^o and ΔG^o reveal that the adsorption process is exothermic and spontaneous.

Mukaratirwa- Muchanyereyi *et al.* [79] used untreated and sulfuric acid treated maize cobs to remove the herbicide atrazine from aqueous solutions. The adsorption studies were carried out in the concentration range of 25 to 100 ppm, pH range of 2 to 10 and temperature range of 30 to 80 °C. The experimental results obtained indicate that pH value of 5 and temperature of 30 °C cause optimum adsorption of atrazine. The experimental data fitted well the Langmuir adsorption isotherm. The removal percentage of atrazine was 99.8 % for acid treated maize cobs and 99.4 % for untreated maize cobs. Thermodynamic parameters, ΔG^o, ΔH^o and ΔS^o were determined and their values suggest the atrazine adsorption is spontaneous and endothermic.

Carbonate-induced activated biochar (CAB) from waste *Calligonum Comosum* biomass has been used as an adsorbent by Alahabadi and Moussavi [80] for the removal of atrazine from aqueous solutions. The maximum atrazine adsorption onto CAB was observed at the neutral water pH. The atrazine adsorption onto the CAB was best fitted with the pseudo-second-order model and the adsorption rate improved with the increase in solution temperature. The equilibrium data fit well to the Langmuir isotherm. The maximum adsorption capacity onto CAB increase from 370.4 mg g^{-1} at solution temperature of 10 °C to 714.3 mg g^{-1} when the solution temperature was increased to 40 °C. The thermodynamic analysis indicated that the atrazine adsorption onto CAB is a spontaneous chemisorption and endothermic process.

Giwa *et al.* [81] studied the adsorption of atrazine using the desert date seed shell activated carbon produced by chemical activation. The batch adsorption experiments revealed that the adsorption of atrazine on desert date seed shell activated carbon was found to be affected by initial contact time, initial atrazine concentration, adsorbent dosage and temperature. The results of the isotherm studies implied that Langmuir isotherm had a better fit. Also, kinetic modeling results obtained showed that pseudo-second order model explained the adsorption kinetics of atrazine by desert date seed shell activated carbon best.

Lu *et al.* [82] studied the adsorption of atrazine in aqueous solutions by sheep manure-derived biochar synthesized at 650 °C (SMB650). They reported that the removal efficiency of atrazine by SMB650 was 95.3 % under the optimum conditions, of which contact time, initial atrazine concentration, initial solution pH, SMB650 dosage and temperature were 150 min, 1500 µg L^{-1}, 3, 1.6 g L^{-1} and 25 ºC, respectively. The results of kinetic and isotherm studies revealed that the pseudo-second order and the Freundlich model fit the experimental data best. The calculated thermodynamic parameters such as energy change (ΔG^θ), enthalpy change (ΔH^θ) and entropy change (ΔS^θ) were -7.8730 to -6.2976, 17.2179 and 0.0788 kJ mol^{-1}, respectively, indicating that the adsorption process of atrazine onto SMB650 was spontaneous, endothermic and entropy-increased.

Cusioli *et al.* [83] studied the adsorption capacity of atrazine by modified Moringa oleifera Lam. seed husks. The best results of atrazine adsorption occurred at pH 5, and the adsorption capacity increased as the pH decreased. The kinetic study indicated equilibrium at 1200 min with an adsorption capacity of 1.90 mg g^{-1} and the best fit was for the pseudo-second order model. The isotherms were obtained at 298, 308 and 318 K. The equilibrium data for atrazine on modified Moringa oleifera Lam. seed husks were modeled with the Langmuir, Freundlich, and Temkin models. The data fitted well with the Langmuir model with a maximum monolayer capacity of 10.32 mg g^{-1}. The values of the thermodynamic parameters indicated that the biosorption was spontaneous, endothermic and reversible.

Yue *et al.* [84] investigated the adsorption of atrazine in three soils (laterite, paddy soil and alluvial soil) by using the batch adsorption experiments. The results revealed that the kinetics of atrazine in soils could be well described by pseudo-second order model. The adsorption equilibrium isotherms were nonlinear and were well fitted by Freundlich and Langmuir models. It was found that the adsorption data on laterite, and paddy soil were better fitted by the Freundlich model; as for alluvial soil, the Langmuir model described it better. The maximum atrazine sorption capacities ranked as follows: paddy soil > alluvial soil > laterite. Results of thermodynamic calculations indicated that atrazine adsorption on three soils was spontaneous and endothermic

Conclusion

This short review paper has attempted to cover a wide range of adsorbents so that the reader can get an idea about the various types of materials used for the removal of atrazine from aqueous systems. There are some conclusions from this short review as following:

- The adsorption process is influenced by some variables governing the efficiency of the process such as the initial concentration of atrazine, contact time, adsorbent dosage, pH and temperature of the medium.
- The adsorption of atrazine was reported to follow Langmuir adsorption model and pseudo-first-order kinetic model in majority of cases.
- The adsorption of atrazine is found to be a spontaneous process ($\Delta G < 0$) and, depending on used adsorbent; this process may be endothermic or exothermic.

Further more interest should be concentrated by the researchers to predict the performance of the adsorption process for atrazine removal from real waters. In addition, 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.

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