

Adsorption of Imazethapyr from Aqueous Solution on Activated Carbon

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The removal of pesticide imazethapyr from wastewater under different batch experimental conditions, using an activated carbon was investigated. The pesticide under study was imazethapyr which is a well known herbicide in Moroccan agriculture. The adsorbent was activated carbon. It was determined that the adsorption of imazethapyr was slightly pH dependent. Different experimental parameters like initial pH, contact time and initial concentration on the adsorption of imazethapyr were evaluated. It was found that the rate of sorption of imazethapyr onto activated carbon is very fast with almost 94 % adsorption taking place in the first 10 min at pH = 3. The applicability of the Langmuir isotherm for the present system has been evaluated at different concentrations.

Key Words: Imazethapyr, Activated carbon, Adsorption, Langmuir.

INTRODUCTION

Water pollution by pesticides from routine agricultural practices is a common¹ and growing problem in the major agricultural areas of the world². Regulations for drinking water are required in order to limit human risks and environmental pollution. World Health Organization (WHO)³ limits pesticides in water to 0.1 g/L for a single pesticide and 0.5 g/L for total pesticides. This class of water pollutants is of particular importance due to toxicity, carcinogenic and mutagenic effects. The removal and disposal of pesticides is an extremely complex problem due to the large range of chemicals that are in use. There is no recognized universally applicable treatment that removes all pesticides. Conventional methods for the removal of pesticides from wastewater include UV treatment, chemical coagulation, sedimentation, filtration, disinfection and sorption onto solid substrates such as activated carbon.

Imazethapyr is used in Moroccan agriculture for weed control in beans, pea and soya¹. It is also an interesting compound since its solubility and its very high mobility in soil and consequently it has high potential to leach^{4,5}. However, this herbicide has a contaminated surface and ground forestry applications⁶. It's interesting to study the removal of imazethapyr from aqueous solution by adsorption processes.

Imazethapyr: [5-Ethyl-2-(4-isopropyl-4-methyl-5-oxo-4,5-dihydroimidazol-1H-2-yl)nicotinic acid] is an imidazolinone herbicide used to control broad leaf weeds and annual

grasses in soybean and peanut⁷. The recent introduction of imidazolinone-tolerant rice varieties allows it to also be used to control red rice and other weeds in commercial rice. Because the use of imazethapyr in commercial rice is relatively new, less is known about its environmental behaviour in flooded rice culture. Imazethapyr is a weak organic acid ($pK_{a1} = 2.1$ and $pK_{a2} = 3.9$), the water solubility of imazethapyr was high (1415 mg/L in distilled water and 3685 mg/L in water buffered at pH 3.9, both at 25 °C). Considering the high water solubility and the low vapour pressure of this herbicide, Henry's law constant (air/water distribution ratio) was calculated to be $2.7 \times 10^{-11} \text{ atm m}^2 \text{ mol}^{-1}$ indicating a high potential for the chemical to remain in water rather than volatilize into the air and vapour pressure $< 0.013 \text{ mPa}$ at 60 °C⁷. The primary dissipation mechanism of imazethapyr in the environment is through microbial degradation⁸. Imazethapyr loss from hydrolysis is minimal, with virtually none observed at pH 5 or 7 and only minimal degradation occurring at pH 9 ($t_{1/2} = 9.6$ months at 25 °C)⁹. Under anaerobic conditions, no significant imazethapyr degradation occurred during a 2-month period when incubated in a variety of soils and sediment⁹. Soil residues of imazethapyr can injure succeeding crops¹⁰⁻¹³.

The term 'activated carbon' refers to a wide range of amorphous carbon-based materials that have been "activated" in order to exhibit a high surface area. Commercial activated carbons are usually derived from natural materials such as coconut shell, wood or coal and are manufactured to produce

precise surface properties. These materials are expensive and require elaborate reactivation and regeneration processes. Such processes often result in the degradation of the adsorption properties of the carbon, which subsequently affects the economic viability of the operation. There is a need for effective but low cost carbons that can be used on a once through basis for a pollution control application that does not require the use of specialized activated carbons.

Activated carbon has versatility and wide range of applications. It has been proven to be an effective adsorbent for the removal of a wide variety of organic and inorganic pollutants from different environments^{14,15}. Activated carbon is classified based on its size shape into four types: powder, granular, fibrous and cloth and each type of them have its specific application as well as inherent advantages and disadvantages in wastewater treatment. Therefore, production of low-cost activated carbon becomes a great goal of many researchers since the commercial activated carbon is still very expensive¹⁴.

The chemical characteristics of adsorbate, such as polarity, ionic nature, functional groups, solubility and the properties of adsorption solution such as pH, concentration of adsorbate, the presence of other species determine the nature of bonding mechanisms as well as the extent and strength of adsorption. Electrostatic and van der Waals forces, H-binding dipole-dipole interactions, ion exchange, covalent bonding, cation bridging and water bridging can be responsible for adsorption of organic compounds in activated carbon¹⁶⁻²².

This paper presents the study of adsorption characteristics of activated carbon powder for removing imazethapyr from aqueous solutions. The binding capacity of activated carbon powder for imazethapyr was shown as a function of contact time, initial pH and initial adsorbent dose in this study. The adsorption equilibrium was expressed by the Langmuir adsorption models.

EXPERIMENTAL

Stock solution was prepared by dissolving 7.225 mg of imazethapyr in 250 mL of distilled water and was stored in a brown colour glass reservoir to prevent photo-oxidation at 25 °C prior to use. The test solutions were prepared by diluting of stock solution to the desired concentrations. The ranges of concentrations of imazethapyr prepared from stock solution varied between the values of 5 and 60 mg/L. The pH of the each solution was adjusted to the required value with 0.1 M H₂SO₄ and 0.1 M NaOH solutions before mixing with the adsorbents to study the effect of pH and the uptake pH was assumed constant during the experiments. The pH-meter using is a Crison pH Meter Basic 20.

Adsorbent: The activated carbon used in this study was provided by the regional laboratory of the National Office of Drinking Water in Morocco. It is a mixture of two types of activated carbon powder which are produced by the company: Fluka Guarantee "Sigma-Aldrich Chemie GmbH".

Adsorbate: The herbicide imazethapyr of analytical reagent grade Riedel-de Haen (purity = 98 %). Deionized water was used in adsorption experiments. Whole optical adsorption spectrum of imazethapyr was recorded and it was seen that λ_{max} of imazethapyr is nearly 270 nm. Absorbance data were

converted into concentrations using calibration line. Adsorption study was repeated on duplicate.

Methods: Specific surface area and pore structure of the activated carbon was determined by using surface area and pore size analyzer (quantachromr, autosorb-1) on nitrogen adsorption (at 77 K). The specific surface area was calculated by the equation of Brunauer, Emmet and Teller (BET)²³. Scanning electron microscopy (SEM) (using Jeol JXA-840 A model scanning electron microscope) analysis to study the surface morphology and to verify the presence of porosity. Size and electrophoretic mobility measurements were conducted using ZetaMeter 3.0 + model zeta Meter (Zeta Meter Inc., Staunton, VA and Portugal). An energy dispersive spectrometer (EDS) was also used to analyze present activated carbon powder.

Adsorption isotherm studies: The measurement of adsorption kinetics of the carbon was carried out by shaking 0.5 g/L of carbon with 50 mL of imazethapyr solution of known concentration in conical flask placed in a thermostat in a shaking flask [the agitation of the engines is carried out using a mechanical agitator model Shaker KS0 (Edmund Bühler; Germany)]. The removal kinetics of the imazethapyr was investigated by taking samples of the solution after the desired contact time and filtered (filtration is carried out using a system of filtration using a nylon filter 0.45 μm Whatman Schleicher and Schuell) and the filtrate was analyzed for its imazethapyr concentration. A spectrophotometer was employed at a wavelength of 270 nm. The pH was adjusted either with 0.1 M H₂SO₄ or 0.1 M NaOH as required. The same procedure has been used to study the effect of initial concentration and pH. The equilibrium isotherm was determined by mixing 0.25 g/L of carbon with 20 mL of imazethapyr solution in a conical flask at the required temperature. Each isotherm consisted of seven different imazethapyr concentrations from 5-60 mg L⁻¹. The flasks containing imazethapyr solutions and carbon were placed in a shaker and agitated for 24 h at the required temperature and at a fixed agitation speed of 150 rpm. The equilibrium concentrations were measured using a spectrophotometer UV-2101 PC Shimadzu.

The equilibrium adsorption uptake, q_e (mg/g) was calculated using the following relationship:

$$q_e = \frac{(C_0 - C_e) \cdot V}{w} \quad (1)$$

where C_0 = initial adsorbate concentration (mg/L), C_e = equilibrium adsorbate concentration (mg/L), V = volume of the solution (L), w = mass of the adsorbent (g).

The concentration of initial and residual imazethapyr was determined by finding out the absorbance of the solution at 270 nm wavelength using UV/vis spectrophotometer (model UV-2101 PC; Shimadzu). The calibration plot of absorbance *versus* concentration for imazethapyr showed a linear variation concentration.

RESULTS AND DISCUSSION

Textural characterization of activated carbon: From the N₂ adsorption isotherm studies, it was found that the BET surface area of the activated carbon is 911 m² g⁻¹.

The adsorbent used in this work was characterized by scanning electron microscope (SEM) (Figs. 1 and 2). These figures show that the adsorbent used has an irregular and porous surface.

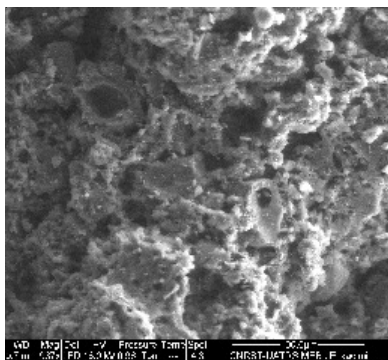


Fig. 1. SEM images of activated carbon powder

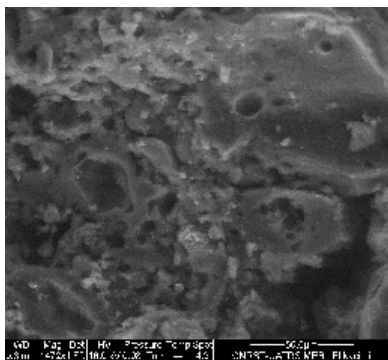


Fig. 2. Porous structure of activated carbon powder

The energy dispersive spectrometer (EDS) analysis provided a rudimentary composition for the activated carbon. The compositions from the peak areas are calculated and shown in Table-1. It was found that carbon, oxygen and silicon were the only common components in the activated carbon powder. Other minor constituents that were determined in the analysis included sulfur, calcium, iron and aluminium.

Element	α	C	O	Mg	Al	Si	S	K	Ca	Fe
Weight (%)		91.04	5.36	0.10	0.57	1.01	0.84	0.16	0.31	0.61

The fractional sieve analysis of the particles is as follows in (Fig. 3).

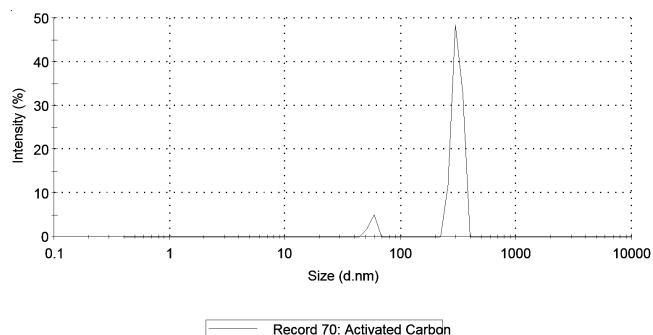


Fig. 3. Size of activated carbon

The fractional sieve analysis of the particles shown in Table-2 is as follows: 307 nm: 93.2 %; 56.7 nm: 6.8 % the Z-average particle diameter was found to be 1570 nm.

Z-average d (nm)	Diam (nm)	Intensity (%)	Width (nm)
1570	307.0	93.2	29.10
—	56.7	6.8	3.52

Characterization of imazethapyr: Some physico-chemical properties of this pesticide are shown in Table-3 and the structure of imazethapyr is shown in Fig. 4.

Chemical formula	$C_{15}H_{19}N_3O_3$
Molecular weight	289.3 g/mol
Physical appearance	Solid
Colour	White to tan
Odor	Slightly nauseous
Melting point	169-173 °C
Vapour	$< 2 \times 10^{-7}$ mm Hg \rightarrow 60 °C
Partition coefficient octanol/water	11 at pH 5, 31 at pH 7, 16 at pH 9
Solubility in water	1415 mg/L at 25 °C at pH = 7
Acid-basic equilibrium	$pK_{a1} = 2.1$, $pK_{a2} = 3.9$

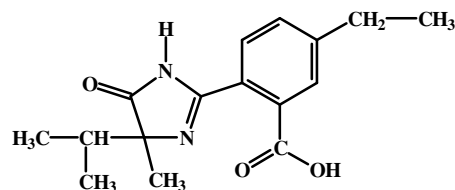


Fig. 4. Structure of imazethapyr

Effect of time of equilibrium: The effect of contact time, between pesticide and adsorbent, needs to be studied first to determine when equilibrium has been achieved. The dependence of adsorption of imazethapyr studied with time is presented in Fig. 5. The analysis of the kinetic curve shows that the adsorption of imazethapyr on the activated carbon is changing rapidly during the first few minutes of contact up to 92 % after a time equal to 10 min.

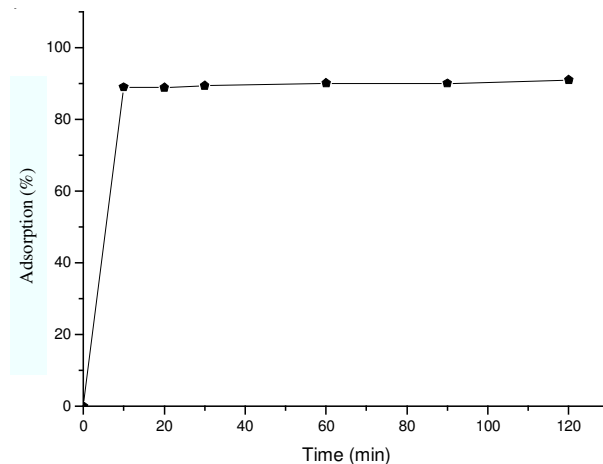


Fig. 5. Effect of time on removal imazethapyr, $C_0 = 30$ ppm, activated carbon dose = 0.5 g/L, pH = 3

The fast of kinetics adsorption, recorded during the first few minutes of contact, can be interpreted by the fact that at the beginning of adsorption the number of the available assets sites to the surface of the material is more important than that of the active sites remaining after a certain time.

Effect of pH: In order to evaluate the effect of pH on the adsorption of imazethapyr on activated carbon, the samples were prepared by wearing contact solution of 30 mg/L of imazethapyr with 0.5 g/L of activated carbon at different pH 2-11. The pH of imazethapyr solution was adjusted from the initial value 7-2, 3, 5, 6, 9, 10.5 by adding either 0.1 M H₂SO₄ or 0.1 M NaOH.

The influence of the pH on the adsorption of herbicide imazethapyr on powder activated carbon as depicted in Fig. 6. It can be observed from the Fig. 6 that the adsorption of imazethapyr increases with pH and reaches a maximum at pH = 3.

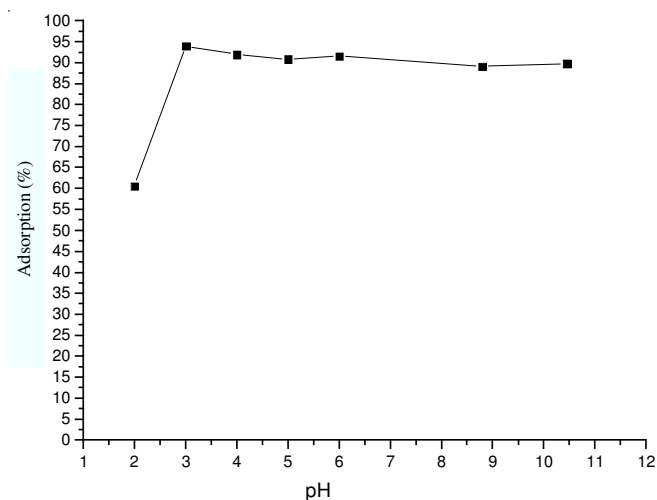


Fig. 6. Effect of pH removal imazethapyr, $C_0 = 30$ ppm, activated carbon dose = 0.5 g/L, time: 10 min

At pH > 3 the per cent of adsorption decreases slight and remain constant. It is conceivable that at low pH 2, where there is an excess of H₃O⁺ ions in the solution a competition excites between the positively charged hydrogen ions and herbicide form 1 of Fig. 7 for the available adsorption sites on the negatively charged of activated carbon surface.

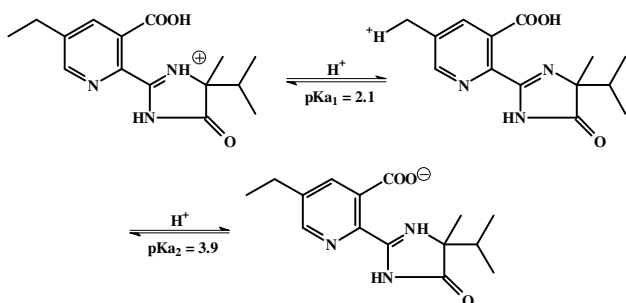


Fig. 7. Variation of imazethapyr form with pH

Effect of activated carbon dosage: Fig. 8 shows the quantity of imazethapyr adsorbed from a concentration of 30 ppm (pH = 3) at various activated carbon dosage, after 10 min of contact.

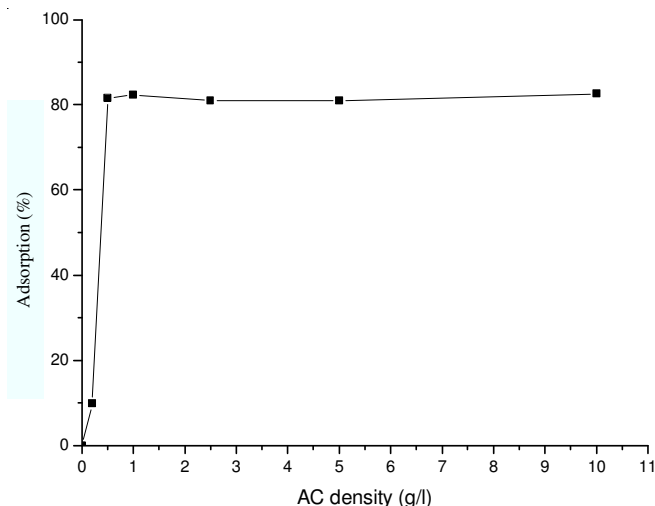


Fig. 8. Effect of powder activated carbon dosage on the sorption of imazethapyr, $C_0 = 30$ ppm, pH = 3, time = 10 min

It was found that increasing the dosage of activated carbon increases the quantity of imazethapyr sorbed from the solution as expected due to the great capacity of the adsorbent. The increase in sorption can be attributed to the increase in external surface area, which, in turn, means an increase in number of available sites for imazethapyr uptake. The external surface area provides more adsorptive sites for the sorption reaction to occur.

Adsorption isotherms: Analysis of the isotherm data is important in order to develop an equation that correctly represents the results and which could be used for design purposes.

The most extensively used isotherm equation for modelling of the adsorption data is the Langmuir equation, which is suitable for monolayer adsorption onto a surface with a fixed number of identical sites and is given by eqn. 2.

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (2)$$

where K_L = adsorption equilibrium constant including the affinity of binding sites (L/mg) and q_{\max} = maximum amount of imazethapyr per unit weight of adsorbent to form a complete monolayer on the surface (mg/g). It represents a practical limiting adsorption capacity when the surface is fully covered with imazethapyr. Q_{\max} and K_L can be determined from the linear plot of C_e/Q_e versus C_e (Figs. 9 and 10). The q_{\max} and K_L thus determined from the Langmuir isotherm were 188.67 mg/g and 0.33 L/mg, respectively at 25 °C. The fundamental characteristics of the Langmuir isotherm have been described by the term separation factor or equilibrium constant R_L , which is defined by Hall *et al.*²⁴ on different systems as, follows:

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

where C_0 = highest initial concentration of adsorbate and K_L is its Langmuir constant. This indicates the nature of adsorption as $R_L > 1$ (unfavourable), $0 < R_L < 1$ (favourable), $R_L = 0$ (irreversible), $R_L = 1$ (linear).

The value of R_L in the present investigation has been found to be 0.0160, showing that the adsorption of imazethapyr is highly favourable.

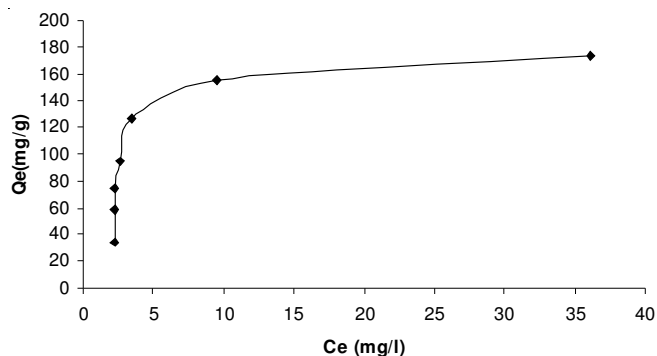


Fig. 9. Adsorption isotherm of imazethapyr onto activated carbon at pH = 3

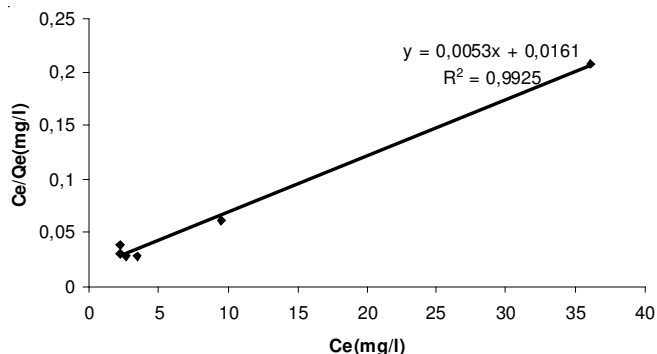


Fig. 10. Langmuir isotherm for imazethapyr adsorption onto activated carbon at pH = 3

Conclusion

The present study shows that activated carbon used is an effective adsorbent for the removal the imazethapyr from aqueous solutions. The maximum removal of imazethapyr is observed up to 94 % at the pH = 3. Adsorption is found to be fast and about 90 % of imazethapyr is achieved in the initial 10 min of contact between activated carbon powder ($m = 0.5$ g/L) and the imazethapyr solution ($C_0 = 30$ ppm) at 25 °C. The equilibrium sorption isotherm data could be well represented

by the Langmuir isotherm equation. The q_{max} and K_L thus determined from the Langmuir isotherm were 188.67 mg/g and 0.33 L/mg, respectively.

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