Banana Peel as an Adsorbent for Removing Atrazine and Ametryne from Waters

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ABSTRACT: The feasibility of using banana peel for removal of the pesticides atrazine and ametryne from river and treated waters has been demonstrated, allowing the design of an efficient, fast, and low-cost strategy for remediation of polluted waters. The conditions for removal of these pesticides in a laboratory scale were optimized as sample volume = 50 mL, banana mass = 3.0 g, stirring time = 40 min, and no pH adjustment necessary. $K_{F(sor)}$ values for atrazine and ametryne were evaluated as 35.8 and 54.1 $\mu g\ g^{-1}$ ($\mu L\ mL^{-1}$) by using liquid scintillation spectrometry. Adsorption was also evaluated by LC-ESI-MS/MS. As quantification limits were 0.10 and 0.14 $\mu g\ L^{-1}$ for both pesticides, sample preconcentration was not needed. Linear analytical curves (up to 10 $\mu g\ L^{-1}$), precise results (RSD < 4.5%), good recoveries (82.9−106.6%), and a > 90% removal efficiency were attained for both pesticides. Water samples collected near an intensively cultivated area were adequately remedied.

KEYWORDS: *banana peel, river waters, treated waters, atrazine, ametryne, water remediation*

■ INTRODUCTION

The pronounced increase in human population during recent decades has led to an enhancement of industrial activity and related environmental problems. As a result of the hostile action taken by mankind to maintain the quality of life, pollution of soil, air, and water bodies is already part of everyday life. Among the degradation that has occurred over the past years, water pollution is one of the utmost concerns.

This environmental problem is mostly related to the food industry and mining and agriculture activities that generate a considerable amount of toxic wastes. In this context, contamination of surface and ground waters by pesticides used in farming has become a serious environmental concern due to the extensive application of pesticides.[1,2] This contamination can be caused by runoff, heap leaching, wind erosion, industrial discharges, etc., and the potential toxicity of the pesticides has motivated continuous research for remediation purposes.[3] Several environmental protection agencies[4−6] provide guidelines to control waste disposal and recommend limiting quantities and concentrations considered to be toxic to terrestrial flora and fauna. It is then advised to establish plans and goals for maintenance and preservation to ensure quality and potability of groundwater reserves and surface waters.

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine) and ametryne (*N*-ethyl-*N*-(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine) have been widely used as pesticides, with selective action in the pre- and postemergence agricultural crops, mainly sugar cane.[7] Due to their high solubility in water, these pesticides may themselves constitute sources of contamination of water bodies.[8,9]

In the European Community, the maximum allowable levels of pesticides in drinking water are 0.1 $\mu g\ L^{-1}$ for each individual substance and 0.5 $\mu g\ L^{-1}$ for the sum of all present pesticides.[5] In Brazil, the maximum allowable concentration for atrazine

was established as 2.0 $\mu g\ L^{-1}$, and there is no recommendation for ametryne.[4]

To remove these pesticides from water, several strategies involving, for example, adsorption, photocatalysis, and/or advanced oxidation processes, have been used.[10] With regard to adsorption, adsorbents of natural origin (e.g., vegetable biomass) have become attractive in view of the availability of abundant supplies, high adsorption capacity, and low cost. This is a remarkable aspect, especially if regional biomass is used.

The use of agricultural waste complies well with the strategies of treatment of effluents with high efficiency and economic viability. Several studies have been carried out to identify new adsorbents for removing heavy metals, colorants, phenolic compounds, and agrochemicals in environmental samples; among them, the bran and rind of rice,[11,12] watermelon rind,[13] wheat bran,[14] carbon sludge,[15] and coal ash[16] have been highlighted. Banana peel has been used as adsorbent for heavy metals[17] and phenolic compounds;[18] application to atrazine was recently reported.[19]

Banana, *Musa* spp, is a worldwide consumed tropical fruit and comprises several varieties, the most cultivated being known as Nanica. The main importers are the United States, Germany, and Japan, and the per capita consumption is higher in some African, Caribbean, and Polynesian countries. In 2007, the annual per capita consumption in Brazil was estimated as 30.76 kg.[20]

Banana peel is the main residue, corresponding to 30−40% (w/w), and has been mainly used in composting, animal feeding, and the production of proteins, ethanol, methane,

pectin, and enzymes.[21−23] Cellulose, hemicellulose, pectin, chlorophyll, and other low molecular weight species are its main constituents.[24] The banana peel presents a high adsorption capacity for metals and organic compounds, and this aspect is primarily due to the presence of the hydroxyl and carboxyl groups of the pectin.[25,26] The adsorption process is the main mechanism of sequestration and involves the accumulation of molecules of a solvent on the inner and outer surface (e.g., pore) of the adsorbent. This process results from interactions among the components involved, namely, adsorbent, adsorbate, and solvent.

In the present work, a novel strategy exploiting adsorption on banana peel is proposed for the efficient remediation of waters contaminated with atrazine and ametryne.

■ MATERIALS AND METHODS

Solutions. The solutions were prepared with reagents of analytical grade quality and deionized−distilled water. Atrazine and ametryne (99.0 and 98.9% purity, respectively) were purchased from Chem Service, Inc. (West Chester, PA, USA). The ^{14}C-radiolabeled molecules (evenly labeled on the ring carbons; specific activity = 3.2 and 1.44 MBq mg^{-1} and radiochemical purity = 95 and 98%, respectively) were purchased from Ciba Geigy (Delhi, India).

Standard stock solutions (10.00 mg L^{-1} of atrazine or ametryne) were prepared by dissolving 10.00 mg in 10.0 mL of acetonitrile. Working standard solutions (0.00, 0.10, 0.25, 0.50, 1.0, 2.5, 5.0, and 10.0 μg L^{-1}) were prepared by successive water dilutions. Acetonitrile (pro HPLC, Spectro, Kleve, Germany), formic acid, and ammonium formate with 99.9, 88.0, and 98.0% purity, respectively, were used for the HPLC operation. The mobile phase consisted of 60% (v/v) acetonitrile and 40% (v/v) aqueous phase (21.7 mol L^{-1} formic acid plus 5.0 mmol L^{-1} ammonium formate).

Samples. River and treated water samples were collected from the Piracicaba and Capivari rivers (S. Paulo state, Brazil) and from the municipal water treatment plant. To this end, a stainless steel container was needed. Thereafter, the samples were transferred to 1 L amber glass bottles previously washed and dried, transported to the analytical laboratories, and stored in coolers with ice.

The banana peels, Nanica variety, were oven-dried (Brasimet, S. Paulo, Brazil) at 60 °C for 5 days, ground (mill frames Deleu, S. Paulo, Brazil), and sieved (stainless steel sieve, 60 mesh). The bromatological and elemental analyses of the banana peels were carried out in the College of Agronomy Luiz de Queiroz, University of S. Paulo. The former relied on van Soest et al.[27] and on AOAC International methods,[28] whereas the latter was carried out according to the method of Zagatto et al.[29]

Apparatus. A LC-ESI-MS/MS chromatographic system (Agilent Technologies, Santa Clara CA, USA) comprised a series 1200 liquid chromatograph, a model 6430 triple-quadrupole mass spectrometer (MS/MS), and an electrospray ionization source (EIS). The chromatographic column was a C$_{18}$ Zorbax Eclipse Plus (3.0 × 100 mm, 3.5 μm) kept at 25 °C. The chromatographic conditions were as follows: flow rate = 0.6 mL min^{-1}; mobile phase, as above specified; injection volume = 10 μL; total run time = 3.0 min; time of recovery = 1.0 min. Under these conditions, the method was validated by verifying the linearity of the analytical curve, working concentration range, detection and quantification limits, repeatability, precision, and accuracy. The ESI source was operated in the positive ionization mode and parameters were set as follows: gas temperature = 300 °C; gas flow rate = 10 L min^{-1}; nebulizer gas, nitrogen (40 psi); applied tension = 4.0 kV. The precursor and product ions were selected in preliminary tests involving variations in the fragmentation and collision energies.[30]

The ^{14}C-atrazine or ^{14}C-ametryne activities were estimated by using a Packard Tri-Carb 1600 TR liquid scintillation spectrometer (Regensburg, Germany). To this end, a 1.0 mL aliquot was taken and added to 10 mL of the scintillation solution. Details of the procedure for radioactivity estimation are given elsewhere.[31]

Other equipments such as a horizontal shaker (Marconi, S. Paulo, Brazil) and an analytical balance were also used.

Pesticide Removal. Atrazine and ametryne removal from waters was accomplished in a laboratory scale by adding the ground/milled banana peel to a preselected volume of water and shaking the resulting suspension during a preselected time interval. The suspension was thereafter filtered (45 μm cellulose acetate filter) and analyzed. The banana mass and the shaking time were varied between 0.5 and 3.0 g and between 20 and 40 min, respectively. Larger banana masses were not tested to avoid an excessive biosorbent amount that would impair the practical applications. In these experiments, atrazine or ametryne was spiked to yield a concentration of 20 or 100 μg L^{-1} in the suspension. The temperature was maintained as 20 ± 2 °C through air-conditioning facilities. The pH of the suspension was either not controlled or otherwise adjusted to 1.5 by HCl addition. These experiments were carried out in a dark environment. Alternatively, atrazine and ametryne were removed from the waters by exploiting a protocol routinely applied to pesticide removal from soils and sediments. The procedure was analogous to that above-described, but water was replaced by a 0.01 mol L^{-1} CaCl$_2$ solution, and a longer shaking period (24 h) was set for equilibrating purposes.

Sorption and Desorption Isotherms. Sorption/desorption experiments for obtaining Freundlich isotherms were carried out in triplicate and involved different (0.100−0.500 μg mL^{-1}) atrazine or ametryne concentrations. A 0.06 g amount of dried and ground banana peel was added to 10 mL of the pesticide solutions prepared in 0.01 mol L^{-1} CaCl$_2$. After shaking, the suspension underwent centrifugation (5000 rpm) during 15 min, and a 1.0 mL aliquot was taken from the supernatant and added to 10 mL of the scintillation solution. The radioactivity of the ^{14}C-labeled pesticides was determined by liquid scintillation spectrometry.[32] The amount of sorbed atrazine and ametryne was calculated as the difference between the initial concentration of pesticide in the suspension and the concentration after the equilibration time.

After collection of the supernatant and determination of the radioactivity in the sorption experiment, the desorption experiment was initialized, involving the same bottles with the banana peels already used in the sorption test. To this end, 10 mL aliquots of the 0.01 mol L^{-1} CaCl$_2$ solution, without atrazine or ametryne, were added to centrifuge tubes containing the remainder banana peels. After shaking and centrifuging, a 1.0 mL aliquot of the supernatant was sampled and its radioactivity was determined. The procedure was replicated once. One can perceive that the procedure was analogous to that involving the desorbed fraction from the sorption experiment. Data were adjusted to the linearized Freundlich equation.

The Freundlich parameters ($K_{F(sor)}$ and N) were estimated from the fitting of nonlinear regression of the equation $C_s = K_F \times C_e^N$ to the experimental data, where C_s = total sorbed concentration (μg g^{-1}), C_e = suspension phase concentration (μg mL^{-1}), K_F (μg g^{-1} or μg mL^{-1})$^{-N}$ = Freundlich distribution coefficient, and N = isotherm nonlinearity factor. Isotherms were obtained by plotting C_s versus C_e, and K_F and N were obtained through nonlinear regression. The linear sorption coefficient (K_d) was estimated by assuming $N = 1$, which was normalized to the organic carbon concentration (OC) of the banana peel. Thus $K_{oc} = K_d$ (OC)$^{-1}$.[33]

Application. The pesticide removal strategy was applied to treated and river waters. For most samples, the pesticides were spiked into the samples to attain pesticide concentrations of about 4 and 10 μg L^{-1}. These experiments were 5-fold replicated. As some river water samples presented too low (<detection limit) pesticide concentrations, pesticide spiking was need.

■ RESULTS AND DISCUSSION

Pesticide Adsorption. Following a 2^3 experimental design, the conditions for pesticide removal from waters by the banana peels were optimized as follows: sample volume = 50 mL of water, banana mass = 3.0 g, stirring time = 40 min. With regard to the suspension pH, it was noted that the pesticide adsorption efficiency underwent a pronounced reduction for pH <5. In

fact, for some acidified samples (pH 1.5, after HCl addition), the adsorption efficiency was halved relative to that attained with 5 < pH < 7. As the pH values of the water samples were >5.0, acidity adjustment prior to the experiments was not required, and design of a simplified and rugged procedure became feasible. It is worthwhile to mention that, under the investigated conditions, the pesticide concentrations did not manifest themselves as a relevant factor influencing adsorption.

Bromatological and Elemental Analysis. Table 1 reveals that the elemental analysis of a typical banana peel matches the

Table 1. Bromatological (Left) and Elemental (Right) Composition of a Typical Blend of Banana Peel[a]

constituent	content	constituent	content
dried material	95	N	1.16
crude protein	8.7	P	0.19
crude fiber	14	K	4.9
ethereal extract	6.2	Ca	0.23
mineral material	13	Mg	0.13
non-nitrogen extract	57	S	0.044
total dissolved nutrients	63	B	24[b]
acidic detergent fiber	23	Cu	3.8[b]
cellulose	14	Fe	45[b]
lignin	9.6	Mn	150[b]
organic carbon	48	Zn	19[b]

[a] Data in % (w/w), dry basis. [b] In mg kg^{-1}.

expected values for plant leaves,[34] with an exception being that potassium was present in a higher concentration. With regard to bromatological analysis, the lignin and cellulose are mostly accountable for the adsorption process[35,36] and the 14 and 9.6% contents were considered to be promising.

Sorption/Desorption Isotherms. Good data fitness was verified after the Freundlich model was applied for data related to the sorption of atrazine and ametryne, as high values for the regression coefficient were noted for both pesticides (Tables 2 and 3). Typical isotherms are shown in Figure 1 and can be described by the following estimated equations:

(a) atrazine sorption: $y = 35.84x^{1.13}$ ($R^2 = 0.992$, $n = 5$)

(b) atrazine desorption: $y = 231.18x^{1.23}$

$$(R^2 = 0.963, n = 5)$$

(c) ametryne sorption: $y = 54.14x^{1.02}$ ($R^2 = 0.994$, $n = 5$)

(d) ametryne desorption: $y = 116.87x^{1.03}$

$$(R^2 = 0.982, n = 5)$$

y = sorbed pesticide concentration in $\mu g\ g^{-1}$, and x = equilibrium pesticide concentration in $\mu g\ mL^{-1}$.

The sorption potential of ametryne by the banana peel was considered to be high,[31] as the $K_{F(sor)}$ value was estimated[32] as
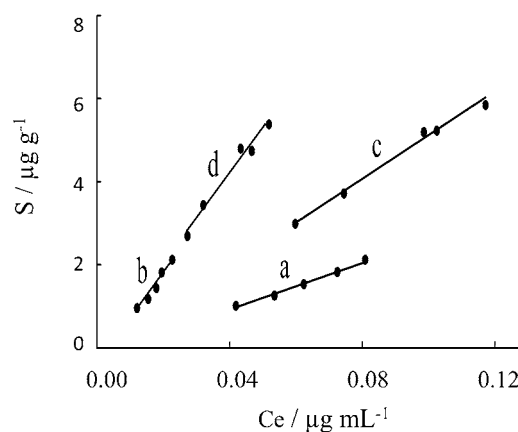
Table 3. Results from Desorption Experiments[a]

pesticide	$K_{F(des)}$ ($\mu g\ g^{-1}$) ($\mu g\ mL^{-1}$)$^{-N}$	N_{des}	R^2	desorption (%)	N_{sor}/N_{des}
atrazine	231	1.23	0.963	47.5	0.91
ametryne	117	1.03	0.982	31.5	1.00

[a] $K_{F(des)}$ = Freundlich coefficient for desorption, N_{des} = degree of linearity, R^2 = coefficient of determination for $n = 5$, N_{sor}/N_{de} = hysteresis index.

Figure 1. Freundlich sorption and desorption isotherms. S, sorbed/desorbed pesticide amount per unit of banana mass; Ce, pesticide concentration under equilibrium conditions; a, atrazine (sorption); b, atrazine (desorption); c, ametryne (sorption); d, ametryne (desorption). For details, see text.

54.1 $\mu g\ g^{-1}$ ($\mu g\ mL^{-1}$)$^{-1}$, which corresponds to 75.3% of the applied ametryne amount. A moderate sorption potential[31] was estimated for atrazine [$K_{F(sor)}$ = 35.8 $\mu g\ g^{-1}$ ($\mu g\ mL^{-1}$)$^{-1}$], corresponding to 59.8% of the applied atrazine amount (Table 2).

The estimates of the distribution coefficients normalized to organic carbon (K_{oc}) for atrazine and ametryne suggest that the increase in adsorption is also related to the quantity of organic matter present in the bioadsorbent, improving the adsorbent/adsorbate interaction.[36]

With regard to the desorption experiments, slightly lower coefficients of determinations were estimated ($n = 5$) for both atrazine and ametryne (Table 3). Nevertheless, the Freundlich model also adjusted satisfactorily to the desorption data.

The sorption and desorption isotherms for atrazine and ametryne were not strictly linear, as the degree of linearity was slightly higher than unity (Tables 2 and 3). When $N > 1$, the isotherms are classified as type S isotherms (sigmoidal).[37] In the present situation, the isotherms approached linearity (Figure 1). The initial adsorption was low and increased with the number of adsorbed molecules. This means that there was an association between the involved molecules, and this synergistic effect can be regarded as a cooperative adsorption.[37] The desorption of ametryne corresponded to 31.5% of the

Table 2. Results from Sorption Experiments[a]

pesticide	$K_{F(sor)}$ ($\mu g\ g^{-1}$) ($\mu g\ mL^{-1}$)$^{-N}$	N_{sor}	R^2	$K_{d(sor)}$ (mL g^{-1})	$K_{oc(sor)}$ (mL g^{-1})	sorption (%)
atrazine	35.8	1.13	0.992	24.8	5.15	59.8
ametryne	54.1	1.02	0.994	50.9	10.6	75.3

[a] $K_{F(sor)}$ = Freundlich coefficient for desorption, N_{sor} = degree of linearity, R^2 = coefficient of determination for $n = 5$, $K_{d(sor)}$ = linear sorption coefficient, $K_{oc(sor)}$ = distribution coefficient normalized to organic carbon.

applied ametryne amount, and this figure was higher (47.5%) for atrazine.

Validation of the LC-ESI-MS/MS. Under the above specified conditions, analytical curves were obtained to validate the analytical procedure. To this end, atrazine or ametryne single-analyte working standards covering 0.00–10.0 μg L^{-1} were used. Typical analytical curves can be described by the following equations:

(a) atrazine: $y = 790x + 26$ ($r^2 = 0.9998$, $n = 8$)

(b) ametryne: $y = 1313x + 19$ ($r^2 = 0.9997$, $n = 8$)

y = analytical signal (counting rate in arbitrary units), and x = pesticide concentration (μg L^{-1}).

A linear relationship between analyte concentration and analytical signal was noted for both pesticides, as the regression coefficients approached unity. Good linearity persisted up to the upper standard concentration (10.0 μg L^{-1}); linearity checking beyond this value is outside the scope of the present work, considering the maximum concentrations found in the water samples collected near intensively cultured agricultural areas.

The detection limits, the lowest analyte concentrations distinguishable from the blank with a certain confidence level (here, 3σ), were estimated as 0.07 and 0.09 μg L^{-1} for atrazine and ametryne, respectively. For σ estimating, the 0.00 μg L^{-1} standard was 10-fold analyzed. The procedure for estimating quantification limits was analogous, but a 10σ confidence level was considered. These figures of merit are presented in Table 4.

Table 4. Analytical Characteristics[a]

pesticide	DL (μg L^{-1})	QL (μg L^{-1})	spiking (μg L^{-1})	recovery (%)	deviation (%)
atrazine	0.07	0.10	0.3	104.0	2.0
			0.6	90.5	3.1
			3.0	82.9	1.4
ametryne	0.09	0.14	0.3	106.6	2.0
			0.6	94.0	4.5
			3.0	85.1	2.2

[a]DL and QL = estimates of the detection and quantification limits.

Recoveries were evaluated by adding atrazine or ametryne (0.30–3.0 μg L^{-1}) to the water samples and comparing the measured concentrations with the expected ones. The experiments were carried out in seven replicates for each concentration. For treated waters, the recovery data ranged from 82.9 to 106.6 (Table 4), and this aspect constitutes itself in an accuracy assessment. These values as well as the deviation are within the range recommended by the European Commission[5] (70% < recovery < 120%, deviation < 20%).

Accuracy was also assessed by adding different standard solutions to river water samples or to buffered acetonitrile solutions (the mobile phase). Very slight variations in results (1.8 and 3.6%) were noted, as similar values were estimated for the angular coefficient of the analytical signal versus added concentration equation, namely, 1313 and 790 counting rate μg^{-1} L (water) or 1290 and 759 counting rate μg^{-1} L (solvent) for ametryne and atrazine, respectively. A noteworthy aspect is that the linear coefficient was only 19 and 26 μg L^{-1} (water) for the pesticides.

Efficiency of Pesticide Removal Efficiency. The efficiency of adsorption by the banana peel was considered to be appropriate; values of 93.8 and 95.2% for atrazine and ametryne in treated waters were similar or even better that those reported elsewhere.[36]

The excellent pesticide removal from treated waters was, however, not verified for river waters. This is probably due to high complexity of river water, which presents a high organic matter content, which may interfere in the adsorption process.[38] Estimating the correlation between organic contents and effectiveness of pesticide absorption involving both Piracicaba and Capivari River water samples is then recommended. Moreover, some chemical species in these water samples probably compete with the pesticides by the active sites of the banana peel, reducing its efficiency as an adsorbent. Moreover, the presence of some pollutants, humic acids, and suspended nanoparticles may play a relevant role in the context. It is hoped that these effects do not inhibit its action, as can be seen in Table 5.

Table 5. Adsorption Efficiency (Percent) for Treated and River Waters

addition (μg L^{-1})	treated water		Piracicaba river water	
	atrazine	ametryne	atrazine	ametryne
4.0	91	93	39	61
4.0	96	96	44	59
4.0	79	85	41	64
4.0	98	96	36	57
4.0	94	95	38	60
10.0	98	98	55	60
10.0	95	97	57	62
10.0	97	98	50	56
10.0	96	98	52	56
10.0	94	96	52	53

It should be finally emphasized that among 10 randomly selected water samples, 7 samples from the Piracicaba river did not present atrazine or ametryne concentrations above the limit of quantification; 3 samples from the Capivari river presented 0.35–0.30, 0.23–0.76, and 0.92–0.53 μg L^{-1} of atrazine and ametryne, respectively; 1 sample collected at the municipal treatment plant showed levels of 0.66 and 0.62 μg L^{-1} of atrazine and ametryne, respectively. After treatment with banana peel, samples from the Capivari River were properly remedied, demonstrating the effectiveness of the proposed treatment. The better efficiency noted for treated waters constitutes itself a positive aspect, as it is mandatory to exclude these pesticides from treated waters to permit its further use.

Application. The experiments carried out in laboratory scale were easily controlled because the sample size was small. As this aspect does not hold for real applications, this limitation should be taken into account for applying this water remediation strategy under field conditions. The banana peel proved to be a suitable biosorbent for atrazine and ametryne removal from waters. High adsorption capacities were observed for both pesticides, and no chemical modifications on the peel surface or pH adjustment was needed. Ametryne showed higher sorption and desorption relative to atrazine in banana peel, as confirmed by the Freundlich isotherms. A very promising aspect of this study is that the biosorbent is easily obtained from a biomass usually regarded as waste and therefore of low cost in the large-scale implementation. It should be finally

stressed that, by using dried banana peel instead of charcoal made from banana peel, the strategy becomes easier in terms of implementation facility and cost.

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Notes

The authors declare no competing financial interest.

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