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Sugarcane bagasse ash for fipronil removal

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ABSTRACT

Adsorbents were studied for removing fipronil, a pesticide, from water. The study included sugarcane bagasse fly ash (SBFA) and traditional activated carbon. SBFA was characterized by X-ray fluorescence, specific mass determination, electron microscopy, particle size analysis and zeta potential. The results showed that, without prior treatment, its removal efficiency for fipronil was 80% with 2 h contact time, which is much higher than reported in other studies. SBFA's zeta potential was 8.02. In low pH systems, fipronil adsorption is expected to be even more efficient, as the molecule presents both the amino group (NH) and Cl, which may favor adsorbent surface interactions by giving rise to polar electrostatic forces. The Freundlich model ($R^2 = 0.9290$) describes the adsorption data better than the Langmuir model ($R^2 = 0.8870$). The method developed for fipronil adsorption is low-cost and enables the reuse of sugarcane industry waste.

Key words: adsorption, alternative adsorbents, fipronil, pesticide removal, sugarcane bagasse fly ash, water treatment

HIGHLIGHTS

- The sugarcane bagasse fly ashes successfully adsorbed fipronil, a potential pollutant of natural waters.
- The removal efficiency was 80% in a contact time of 2 h.
- The use of the ashes is quite favorable when compared with commercial activated carbons.
- The developed method is low-cost and comprises the recycling of waste from the sugar and ethanol industry.

GRAPHICAL ABSTRACT
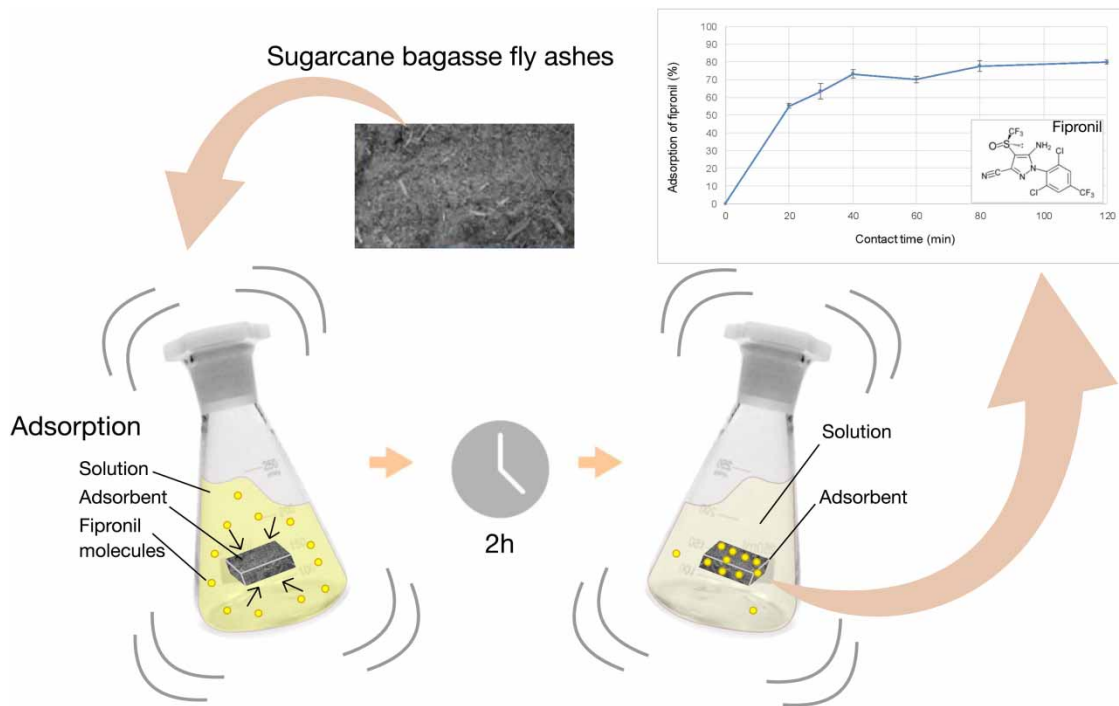
INTRODUCTION

The scientific consensus is that many pesticides, even in trace concentrations ($\mu g\,L^{-1}$ or $ng\,L^{-1}$), represent a potential risk to aquatic biota and human health. Their adverse effects on human health can be acute or chronic. Acute effects, at high concentrations, include favoring alterations in biological functions or even death. Chronic effects, at lower concentrations and with long exposure times, manifest as uncontrolled cell growth, leading to malignant tumors, mutagenic effects – with heritable changes in cell genetic material – and/or teratogenic effects, causing non-hereditary congenital deformations.

There is evidence that conventional water treatment involving chemical coagulation, flocculation, sedimentation or flotation, and rapid filtration is not very effective in removing pesticides. This is probably because the coagulants usually employed are ineffective in destabilizing and precipitating these compounds, so that separation in subsequent treatment steps is not possible. Selective adsorption may occur, onto clay particles that confer turbidity to natural waters, with their subsequent removal in sedimentation, flotation or filtration stages. In this scenario, adsorption is a complementary treatment step to remove pesticides from water for human consumption. Powdered activated carbon (PAC) of plant, mineral or animal origin is the most widely used adsorbent for this purpose in developing countries. The application of granular activated carbon, as the last step before disinfection, is more commonly seen in developed countries, to remove the precursors of chlorination byproducts.

However, the high cost of activated carbon often makes its use in water treatment infeasible, especially for small systems. For coconut shell-based activated carbon produced in Brazil, for instance, a dose of around $10\,mg\,L^{-1}$ is estimated to cost approximately US\$3.2/100 m^3-treated, approximately 60–70% of the total cost of the water treatment chemicals.

The number of studies involving natural materials or industrial waste as adsorbents has been increasing recently. Several natural adsorbents – e.g., *Jatropha curcas*, cassava bark, Brazil nuts, cashew nuts and pinus bark, cattail (*Typha angustifolia*), natural bushing (*Luffa cylindrica* fruit), coconut fiber, silk cotton rice husk ash and *Moringa oleifera* seeds (Gomes *et al.* 2022) – have demonstrated pesticide adsorption efficiency from water.

Characteristics and toxicity of fipronil

Of the pesticides that can cause harm to health, 40 are included in the Brazilian drinking water standards (Regulation 888 2021), 97 in the US standards (USEPA 2019) and 149 in the Australian standards (Araújo 2018). In Brazil, 15 pesticides (including fipronil) are mentioned in the drinking water standards. Fipronil (5-amino-1-[2,6-dichloro-4-(trifluoromethyl) phenyl-4-(trifluoromethylsulfinyl)-1H-pyrazole-3-carbonitrile) is an insecticide in the phenyl pyrazole chemical group. Classified in toxicological class II, it is considered highly toxic and is easily found for sale in various formulations (emulsions, granules and powders).

Fipronil acts specifically on insect central nervous systems, blocking chloride channels regulated by gamma aminobutyric acid receptors, causing paralysis and death (Bae & Kwon 2020). The insecticide is widely used in agriculture, in foliar treatment on cotton and soybean crops, and in soil treatment in potato, sugarcane and corn crops. It is also used in veterinary medicine to control a wide variety of insects, including cockroaches, mosquitoes and fleas (USEPA 2019; Bae & Kwon 2020).

Fipronil is highly toxic to non-target organisms including lizards (LC_{50} for *Acanthodactus dumerili* $30\,\mu g\,g^{-1}$ body weight) and poultry ($LC_{50} = 11.3\,mg\,kg^{-1}$ quail). However, it has low toxicity to waterfowl ($LC_{50} > 2{,}150\,mg\,kg^{-1}$ mallard) and moderate toxicity to mammals by oral exposure ($LC_{50} = 97\,mg\,kg^{-1}$ for rats; $LC_{50} = 91\,mg\,kg^{-1}$ for mice) (Tingle *et al.* 2003). There are few reports of poisoning in humans. In studies of acute exposure in mammals, fipronil showed high toxicity through the gastrointestinal tract. Chronic exposure in rats led to convulsions (sometimes death), decreased body weight, and hematological and biochemical changes – e.g., in cholesterol, calcium, proteins and hormones. Fipronil was carcinogenic in male and female rats, producing benign and malignant thyroid tumors at higher doses (Tingle *et al.* 2003).

Fipronil is hydrolyzed at slightly acidic to neutral pH but degrades with a half-life of 28 days in more basic solutions (pH ≈ 9). In soil, when exposed to light, it degrades slowly, with a half-life of 34 days (USEPA 2019). One of the main degradation products is fipronil desulfinil, which is generally more toxic than the original compound and very persistent (Tingle *et al.* 2003). Figure 1 shows the dissociations of fipronil into fipronil sulfide, fipronil desulfinil, fipronil sulfone and fipronil amide, by reduction, photolysis, oxidation and hydrolysis, respectively.
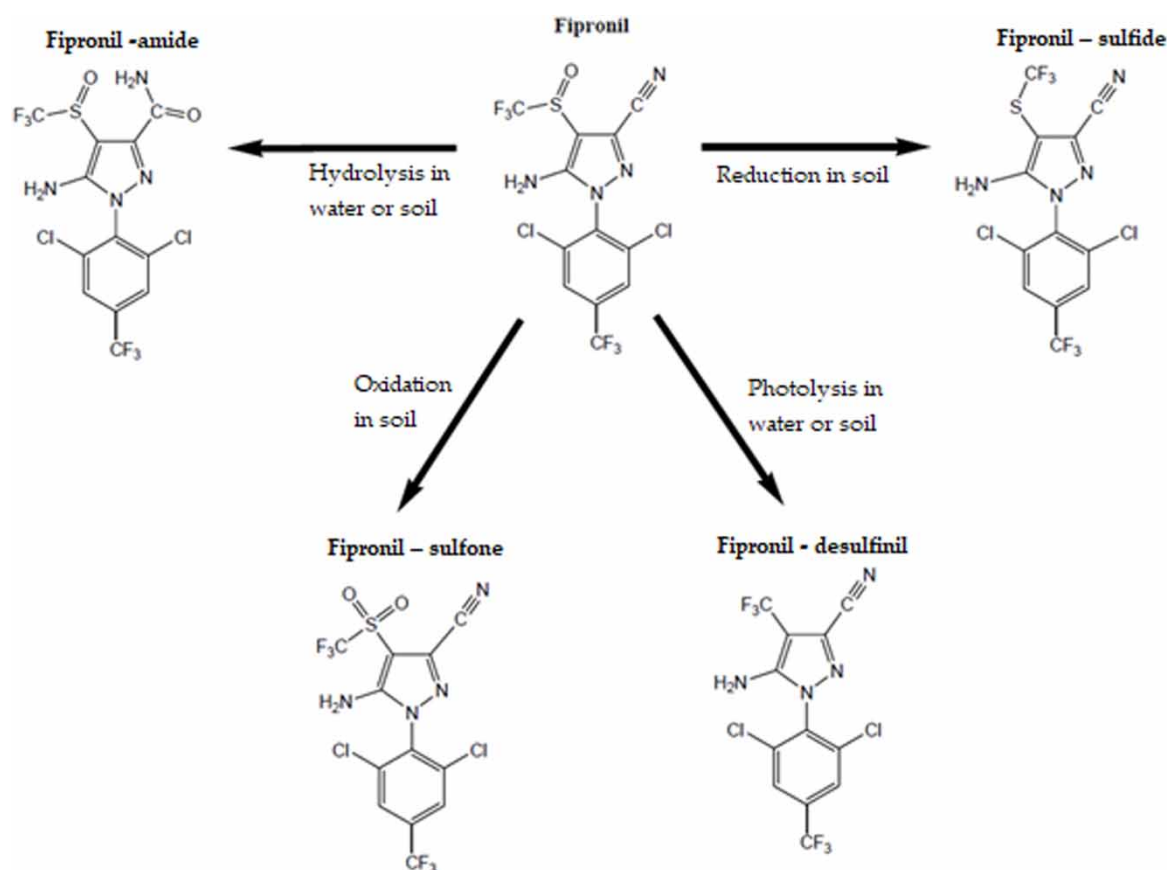

Figure 1 | Dissociations of fipronil in soil and water.

Studies have shown high acute fipronil toxicity in 96 h to several fish species, and induces physiological altera-tions, affecting larval growth, with a 'no observed effect concentration' (NOEC) of 0.0066 mg L^{-1} and an 'observed effect concentration' (OEC) of 0.015. It has also been shown to be toxic in studies with freshwater invertebrates including *Daphnia magna*, oysters, shrimps and aquatic plants (USEPA 2019; Dallarés *et al.* 2020).

The concentrations of several pesticides were evaluated in the Brazilian rivers Vacacaí and Vacacaí-Mirim, in Rio Grande do Sul State, in the harvests from 2005/06 to 2007/08. In the Vacacai in 2005/06, at least one pes-ticide was found in 94% of samples, fipronil, carbofuran and imazethapyr having the highest proportional detection rates. The Vacacaí-Mirim had the highest fipronil concentrations in its samples. Fipronil stood out in the 2006/07 season as the only pesticide detected in all samples. Fipronil concentrations varied from 0.05 to 26.20 μg L^{-1} in the 2005/06 and 2007/08 harvests (Marchesan *et al.* 2010).

The occurrence of fungicides and pesticides was evaluated in surface- and groundwaters, and sediment, in Idaho, Maine and Wisconsin in the USA, and fipronil was found in 8% of the groundwater samples at concen-trations of about 2.2 ng L^{-1} (Orlando *et al.* 2009). Fipronil sulfide was present in 5% of the sediment samples, at a concentration of 1.4 μg kg^{-1}. Previously, fipronil and three degradation products – fipronil desulfinil, fipronil sul-fide and fipronil sulfone – in the Mermentau River basin in Louisiana, with surface water concentrations of between about 0.83 and 5.26 μg L^{-1}. The predominant degradation product in the sediments was fipronil sulfide, with concentrations of 0.64–24.80 μg kg^{-1}.

Fipronil's toxicological characteristics and frequency of appearance in water bodies led to its inclusion in the recent Brazilian drinking water standards (Regulation 888 2021) with a maximum permissible concentration of 1.2 μg L^{-1}. Internationally, only the Australian standard exceeds this with a limit of 0.7 μg L^{-1}, although, until 2017, no studies indicated the presence of fipronil in Australian water bodies (Araújo 2018).

Alternative adsorbents

Microcontaminant molecules adsorbed onto an empty surface are held by forces from the adsorbent surface. If the attraction is physical, the process is classified as physical adsorption or physisorption. Generally, in this, the attraction arises from van der Waals forces, which are weak so the adsorption is reversible. If chemisorption – i.e., chemical bonding – is involved, however, by electron rearrangement or sharing, a monolayer forms on the adsor-bent surface, which is practically irreversible.

Natural materials – *Moringa oleifera* seeds, jatropha, cassava, rice husks, different types of nuts, vegetable loofah, etc. – have been used to adsorb organochlorine and organophosphorus pesticides and trace metals (Cd, Pb and Cr), sometimes without any prior chemical treatment (Rodrigues *et al.* 2014). In the wider context, some wastes, industrial byproducts or low-cost synthetic materials – e.g., slag, boiler ash, sugarcane bagasse, red mud, etc. – have been used as adsorbents. Almeida *et al.* (2020) showed that enrichment of polyurethane foams with petroleum industry catalyst waste (20–80% by weight) increased their adsorption capacity for high concen-tration trifluralin pesticide (30 mg L^{-1}) in synthetic waters. The highest removal results (95.3%) were achieved using only the catalyst residue as an adsorbent.

Increased global demand for ethanol from renewable sources, associated with large cultivable areas and favor-able climatic conditions, have made Brazil the world's largest sugarcane producer. Some 654,839 tonnes of sugarcane were processed for sucrose and ethanol production in 2019/2020 (Conab 2017), making SBFA one of the most abundant industrial wastes in the country. On average, 1 tonne of sugarcane produces 280 kg of bagasse, with about 50% moisture content. Bagasse is usually burned to generate energy for industry, making bioelectricity from sugarcane the fourth source in the Brazilian energy matrix (Canilha *et al.* 2012).

SBFA, as a by-product of the sugar and alcohol industry, has great potential as an adsorbent in water and wastewater treatment (Sarker *et al.* 2017; Yadav & Singh 2020). This arises because its main components – alumina, silica, ferric oxide, calcium oxide, magnesium oxide and carbon – and physical properties, such as porosity, particle size distribution, specific surface and alkaline nature (Ahmaruzzaman 2010). Quite extensive research has been done on sugarcane bagasse ash as an adsorbent for removal of metal ions – Zn^{+2}, Cu^{+2} and Cr^{+3}, Ni^{+2}, Cd^{+2} and Pb^{+2} – drugs, acetylsa-licylic acid and diclofenac (Shah *et al.* 2011; Ferreira *et al.* 2015; Salomão *et al.* 2019; Rodríguez-Díaz *et al.* 2021).

METHODS

Characterization of SBFA

The SBFA was provided by the Minas Gerais Sugar-Energy Industries Association and generated in a plant in the state. The ash was characterized according to its carbon, metal and oxide content, and specific mass. Total

organic carbon (TOC) was quantified using an SSM-5000[a] module coupled to a Shimadzu TOC-L CSH/CSN instrument. The determination was made by the indirect method, with total carbon measured from the catalytic oxidation at 900 °C to CO_2 of all carbon present. Inorganic carbon was measured after acid-purging the CO_2, and the TOC value obtained as the difference between total and inorganic carbon (Adarme 2018).

Soluble metals and metalloids – i.e., Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sn, Sr, Ti, V and Zn – the EPA 3050B methodology was used (USEPA 1996). Initially, a 1.5 g ash sample (moisture content 8.3%) was subjected to partial acid digestion before subsequent analysis by inductively coupled plasma optical emission spectrometry (ICP-OES) (Adarme 2018).

Oxides, including SiO_2, Al_2O_3, Fe_2O_3, TiO_2, MnO, MgO, CaO, K_2O and P_2O_5, were determined in an X-ray fluorescence spectrometer (Philips Panalytical MagiX with a PW2540 autosampler and a 2.4 kW rhodium tube). The spectrometry pellets were constructed from 2.5 g ash samples (undigested solids) with 1.0 g of binder. The calcination loss (%) was calculated gravimetrically after heating the sample to 1,050 °C for 60 min.

Specific mass was determined using the ABNT NBR 6458:2017 procedures (ABNT 2017). The sample density was determined gravimetrically in triplicate, by weighing 125 g of it, placing it immediately in a calibrated, 500 mL pycnometer, and applying a vacuum (88 kPa) for 60 min (Adarme 2018).

Ash surface morphological properties were determined by the scanning electron microscopy (SEM), using a TESCAN VEJA 3 electron microscope coupled to an Oxford microanalysis system. This provided the adsorbent's particle shape and texture.

Particle size analysis was performed with a vibrating sieve and Tyler/Mesh series sieves. The material was weighed with a Shimadzu AUX220 digital balance – resolution 0.0001 g maximum capacity 220 g. Sieving time was 5 min for all tests in a set of five sieves (0.038–0.300 mm, 400–48 mesh), with no openings in the bottom unit. The material retained on each sieve was weighed after sieving, and the tests were performed in triplicate with initial masses of 15.0040, 15.0131 and 15.0072 g. The aim was to identify the material's most representative diameter, so the sieve retaining most material indicated the predominant granulometry and was adopted as the standard granulometry in the adsorption tests.

Point of zero charge determination

The point of zero charge (PZC) was determined using three distilled water matrices prepared for pH values 3, 6 and 11, each divided into seven, 20 mL aliquots. pH was adjusted with nitric acid and 0.1 M sodium hydroxide solutions. Different, known amounts of ash were added, yielding seven Erlenmeyer flasks for each pH. The 21 flasks were stirred constantly at 118 rpm and 35 °C to reach equilibrium pH, and the final pH in each flask was measured. Plots of pH versus ash content were used to determine PZC graphically.

Adsorption tests

The 1.0 g-fipronil·L^{-1} solution was prepared in methanol and stored at −20 °C to minimize degradation. Fipronil, diluted in methanol, was stirred into the study water in a 2 L flask for 10 min, before 100 mL aliquots (20 μg-fipronil·L^{-1} in water) were transferred to seven conical flasks, which received fixed masses – 1.0–7.0 mg, in 1 mg steps – of the adsorbent. 100 mL of the study water and 2.0 mg of adsorbent were placed in another flask as a control. The experiments were performed in triplicate using groundwater at pH 7.2.

The Erlenmeyer flasks were shaken at 145 rpm and 25 °C for 60 min, after which, 10 mL samples were taken from all flasks. The samples were filtered under positive pressure using a Millipore 0.22 μm membrane. Finally, 150 μL aliquots were transferred to vials and stored in a freezer prior to HPLC-MS/MS analysis. After the assays, the Langmuir, Tempkin and Freundlich isotherm models were used to fit the fipronil adsorption data.

Determination of the equilibrium condition enables the maximum adsorption capacity under controlled conditions to be inferred. The same stock standard fipronil solution was mixed with the study water, with 10 min contact time. 100 mL aliquots of the 20 μg-fipronil·L^{-1} solution were transferred to Erlenmeyer flasks and equal (60 mg L^{-1}) adsorbent doses added. 60 mg-adsorbent·L^{-1} was determined as the optimum for fipronil removal in the adsorption tests, and fixed contact times of between 20 and 120 min were used. A blank test – with no adsorbate – was also run. All other test conditions were the same – i.e., shaking at 145 rpm at 25 °C, filtration under positive pressure on a 0.22 μm membrane, etc.

Adsorption tests were also done using commercial PAC of vegetable origin, under the same conditions defined for the ashes, to compare the adsorbents. A 20 mg-PAC·L^{-1} dose and the same fipronil standard stock solution were used.

Experimental tests

The tests with both SBFA and PAC were done using water treated with clay and calcium hydroxide (10% m/m). Similar water pH and turbidity characteristics – about 7.3 and 140 uT, respectively – to the influent raw, rainy season water to a large conventional treatment plant (average inflow about 5.8 m^3 s^{-1}). The jar test equipment could provide velocity gradients of about 10–2,000 s^{-1} (Figure 2).

Figure 2 | Jar test equipment with ash dispersion in three flasks.

There were three phases in the jar test assays. Phase I corresponded to the application of 60 mg-SBFA·L^{-1} and 20 mg-PAC·L^{-1}, in three flasks for each adsorbent. The hydraulic parameters in this phase reproduced those in the treatment plant noted above – i.e., rapid mix velocity gradient 800 s^{-1} ($\sim$400 rpm), agitation time 5 s, flocculation velocity gradient 35 s^{-1} ($\sim$40 rpm), flocculation time 10 min and settling velocity 6.0 cm min^{-1} (sedimentation time $\sim$70 s).

The remaining turbidity was determined in the six samples after settlement before the samples were filtered under positive pressure on a 0.45 μm membrane. Subsequently, 150 μL aliquots were stored in a freezer prior to fipronil analysis by HPLC-MS/MS.

In Phase II, fipronil removal by ash (3 vials) and without adsorbent was compared, using the same dose of aluminum sulfate (100 mg L^{-1}) in all flasks. The methodology was the same as in Phase I, except that flocculation time was 40 min, which was adopted following indication from the tests of maximum fipronil removal at this contact time.

Finally, in Phase III, using the same procedures as in Phase II, the adsorbent was changed to PAC (at 20 mg L^{-1}) and flocculation time to 20 min.

RESULTS AND DISCUSSION

Chemical XRF spectrometry analysis

The chemical composition of SBFA is shown in Table 1.

Table 1 | Composition of SBFA

| Chemical species	Proportion (%)
Lost on calcination	43.7
SiO_2	25.04
Al_2O_3	7.84
Fe_2O_3	7.83
K, Ca, Mg, P, Ti, Mn, Na oxides	15.59

As shown in Table 1, the loss on calcination (LC), which represents the carbon not lost as CO or CO_2 during sugarcane combustion, was approximately 43.7%. This remaining carbon could provide adsorptive capacity, and its amount depends on both the proportion of water in the bagasse and the efficiency of its combustion.

In addition to the high residual carbon content, the predominance of silicon oxides, accompanied by aluminum and iron oxides, is noted. The presence and chemical characteristics of such oxides favor the accumulation of surface hydroxyls, which can contribute to specific interactions with the adsorbate. Thus, hydrogen bond-type intermolecular interactions probably contribute to organic compound removal. For fipronil, hydrogen bonding interaction could arise between the surface hydroxyls and the amino group (NH_2) present in the pesticide.

Morphological properties (SEM)

Figure 3 shows an SEM image of SBFA (500×), showing a heterogeneous morphology, with a fibrous and irregular crack-like structure.

The fibrous particles are linear and skeletal, with holes and threads, as reported by others (Rodríguez-Díaz et al. 2015; Sarker et al. 2017; Mor et al. 2019). The irregular particles were caused by the melting and solidification of
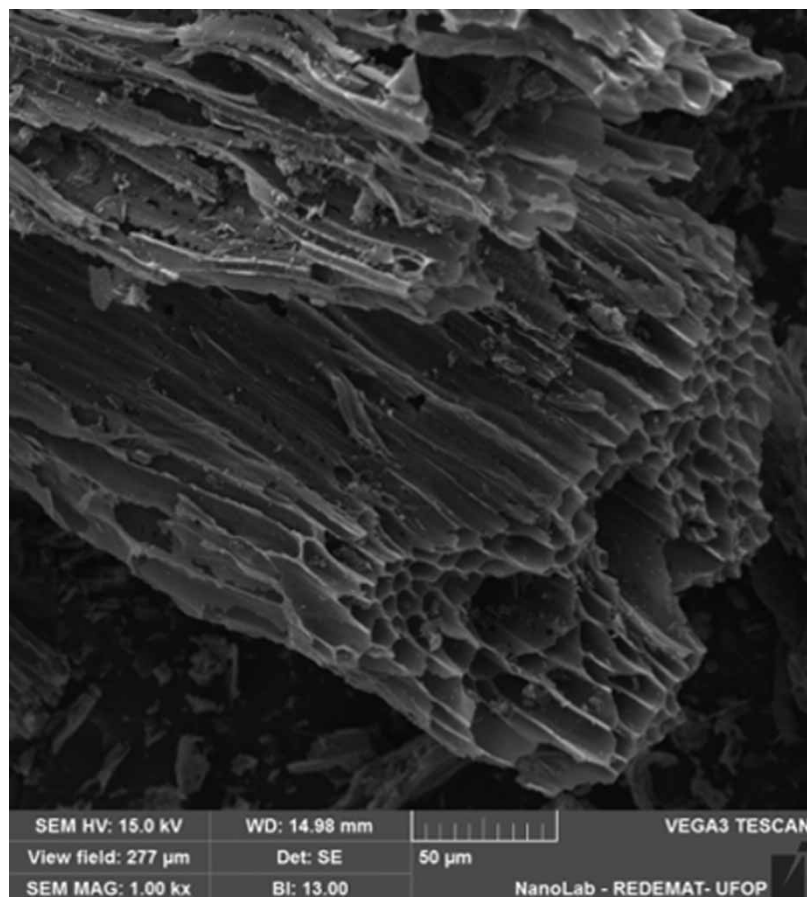
Figure 3 | SEM image of SBFA (500×).

the oxides of silicon and metallic elements during combustion. The large amounts of silicon and oxygen corroborate the high SiO_2 content found in the XRF analysis. In this context and given the ability of surfaces with high silica content to enable the ion exchange of metallic species, it is advantageous for its use as an adsorbent (Shah et al. 2011). Similar morphologies were observed in other sugarcane bagasse ashes (Rodríguez-Díaz et al. 2015; Sarker et al. 2017; Mor et al. 2019; Toledo-Jaldin et al. 2019; Yadav & Singh 2020; Kumari et al. 2021).

Granulometric tests

Figure 4 shows the particle size analysis results for the three SBFA samples. Most of the material had a particle diameter < 200 MESH > 400 MESH, so this particle size range was used in all adsorption tests.
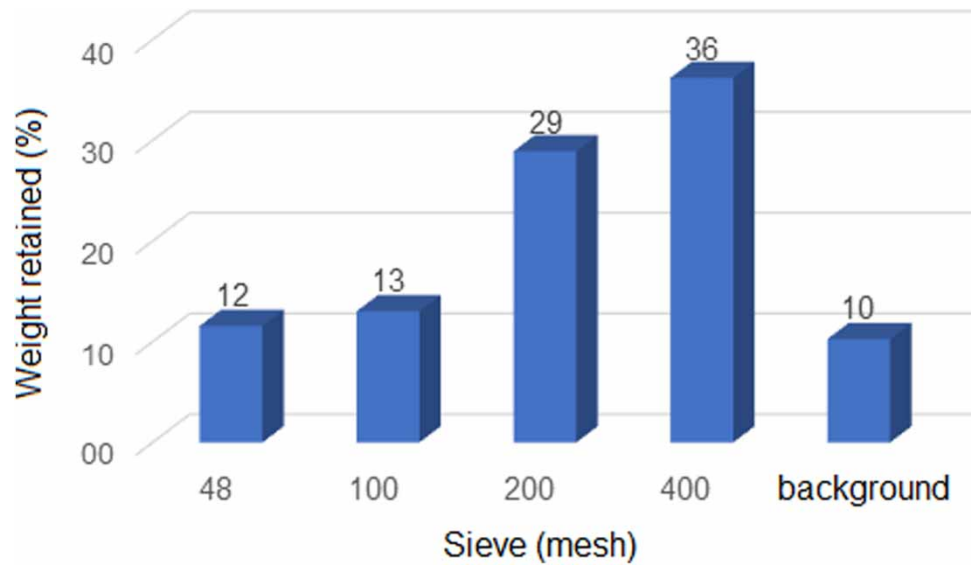

Figure 4 | Granulometric analysis of SBFA.

PZC determination

The PZC is the pH at which the charge on the adsorbent surface is zero, and was determined as 8.02 for SBFA (Figure 5(a)). This accords with studies by Rodríguez-Díaz et al. (2015). Thus, it is assumed that the ash surface is positively charged when the pH is below 8.02 and negatively charged above that.
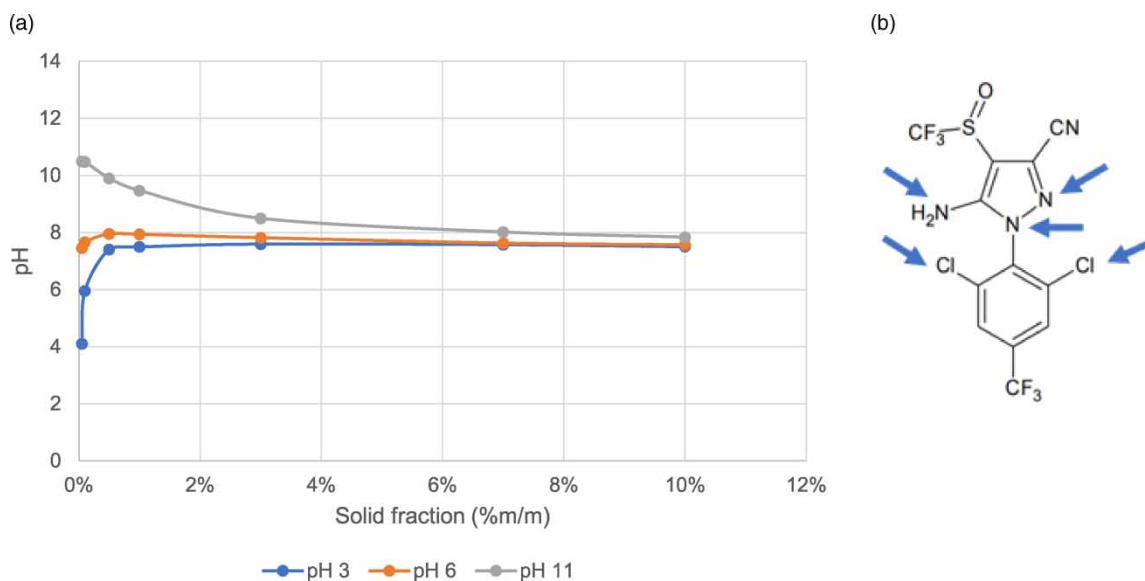

Figure 5 | Measurements of SBFA's isoelectric point.

In application of SBFA in water treatment plants, where coagulation pH values are generally around 6.2–6.8, the ash surface charge is expected to be predominantly positive, which may favor electrostatic interactions between negatively charged species and the adsorbent. This seems to be related to changes in the SBFA's surface charges, and the ionization of atoms or groups of molecules, facilitating the adsorption mechanisms. Therefore, at low pH, ionization of nitrogen atoms, chlorine and/or NH groups of the fipronil molecule is likely to occur (Figure 5(b)).

Adsorption

Isotherms

Fipronil concentration in solution was determined by liquid chromatography. Figure 6(a) shows that 60 mg-SBFA L^{-1} achieved 85% fipronil removal and the adsorption isotherm reported a maximum adsorption capacity of 0.738 ug·mg^{-1} (Figure 6(b)).
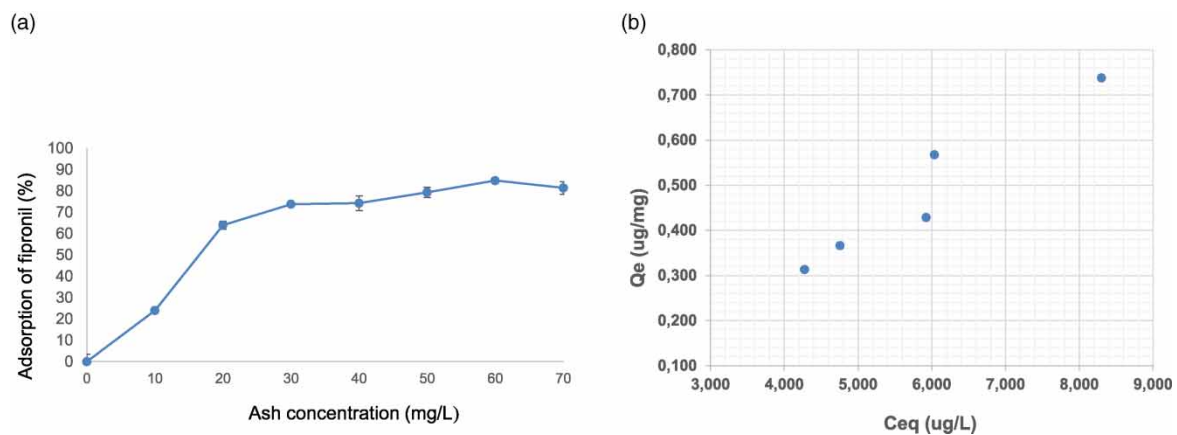

Figure 6 | Fipronil removal versus amount of adsorbent (mg L^{-1}) (a) and adsorption capacity versus fipronil equilibrium concentration (b).

The parameters obtained by adjusting the Langmuir and Freundlich models are presented in Table 2.

The isotherm R^2 values show that the Freundlich model ($R^2 = 0.9290$) describes the adsorption data better than the Langmuir model ($R^2 = 0.8870$). The isotherm result of this study is in accordance with the literature (Yadav & Singh 2020).

Table 2 | Estimated fipronil adsorption/SBFA parameters using the Langmuir and Freundlich models

Parameter	Model	
	Langmuir	Freundlich
KL (L · mg^{-1})/KF	0.02987	0.05088
RL/n	1.01659	0.78892
R^2	0.8870	0.9290

Although the value of 'n' is <1 (0.8), SBFA performs better than commercial PAC, especially considering, among other things, the economic and environmental factors.

The Freundlich model indicates that the ash may present a heterogeneous surface with adsorption occurring in multiple layers. A plausible explanation for this is the hydrogen interactions generated between the surface hydroxyls present on the ash and the NH$_2$ group present in the fipronil molecule.

Contact time

Figure 7 shows the influence of contact time between SBFA and the fipronil solution.
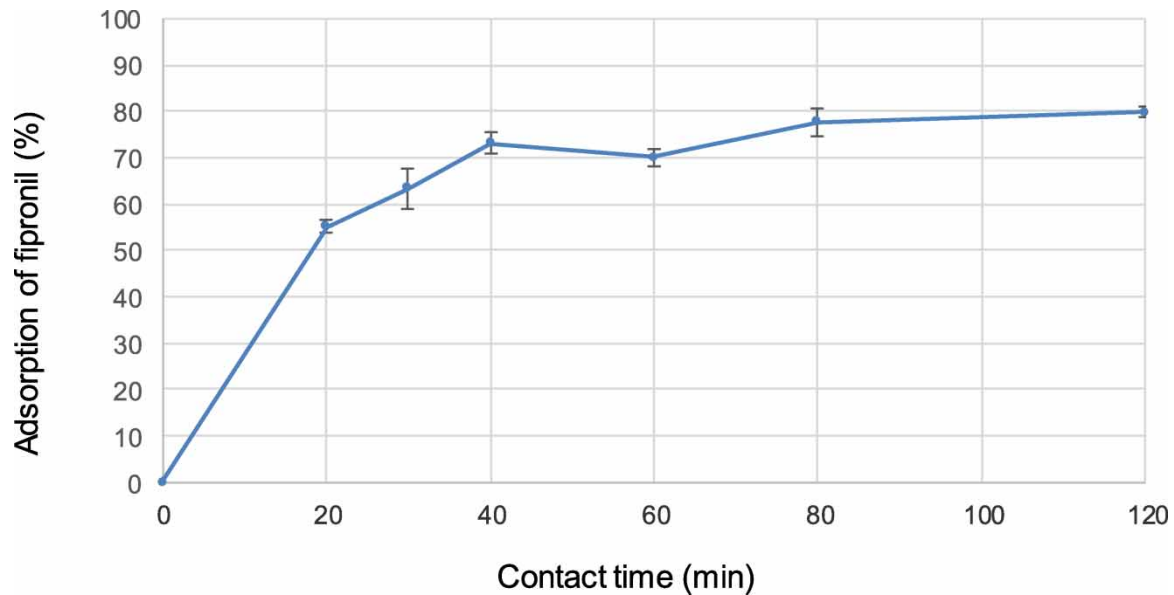
Figure 7 | Fipronil removal (%) versus contact time with SBFA.

As can be seen, fipronil adsorption capacity increased rapidly for the first 40 min, achieving 73% efficiency. Subsequently, the rate slowed until saturation was reached. The highest efficiency observed was just below 78% at 80 min contact time. This is slightly higher than that obtained by Yadav and Singh – about 76% in 24 h – in their study (2020). It should be noted that very long contact times – e.g., 24 h – are infeasible in municipal-scale water treatment.

The contact time for fipronil removal acquires relevance in relation to the use of SBFA in conventional water treatment plants. Such plants – equipped with rapid mix, flocculation, sedimentation and filtration units – supply approximately 75% of Brazil's population, a proportion that increases to 94% when considering only surface water sources (Libânio 2016). As adsorbent application, usually PAC, usually occurs in the rapid mix unit, the theoretical contact time, in the plant, is about 2–3 h.

Adsorption with PAC

PAC adsorptive capacity was evaluated by comparing the fipronil concentration in the aqueous medium before (control) and after addition. PAC's fipronil removal efficiency was 79% for 20 min contact time, rising to 97% with 120 min contact time. In other words, it exceeded SBFA's fipronil removal efficiency in all situations studied. Nevertheless, while SBFA's performance (60 mg·L^{-1} dose) has been 17% lower on average than PAC's (20 mg·L^{-1} dose), it is noted that PAC's cost is much higher than that of SBFA (Varsha *et al.* 2022). The costs of the chemical products usually applied in water treatment are approximately US\$1.6–2.0/100 m³. Due to Brazil's continental dimensions, which significantly increase transport costs, this estimate was based on water treatment plants in the country's Southeast Region, the richest part and home to approximately 44% of the Brazilian population. The rare use of PAC in water treatment plants in Brazil and developing countries is largely due to the high cost. Assuming an average applied dose of 10 mg L^{-1} and the use of coconut shell activated carbon (US\$3.0/kg), the cost would be around US\$3.2–3.5/100 m³. Thus, PAC application will increase the cost of treatment chemicals by approximately 200–275%, in addition to personnel and electricity costs (Libânio 2016).

CONCLUSIONS

A number of conclusions can be drawn from the results of this study:

(i) SBFA were successfully shown to adsorb fipronil, an insecticide and potential pollutant. SBFA use is quite favorable compared with commercial PAC, especially in the context of economic and environmental feasibility.

(ii) Although SBFA's removal efficiency is lower than that of PAC, it is a viable solution, because, without prior treatment, its removal efficiency was almost 80% with an hour contact time.

(iii) SBFA's low fipronil removal contact time is especially relevant in relation to the material's use in full-scale conventional water treatment plants, where the theoretical contact time is about 2–3 h.

(iv) It is likely that fipronil adsorption is more efficient in low pH systems, since the fipronil molecule presents the amino group, which may favor surface interactions on the adsorbent by giving rise to polar electrostatic forces.

(v) The isotherm R^2 values showed that the Freundlich model ($R^2 = 0.9290$) describes the adsorption data better than the Langmuir model ($R^2 = 0.8870$).

(vi) Finally, the method developed is low-cost and efficient, and comprises the reduction, reuse and recycling of sugar and ethanol industry waste, promoting the circular economy and therefore sustainability.

ACKNOWLEDGEMENTS

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

REFERENCES

ABNT – Associação Brasileira de Normas Técnicas. NBR 6458 2017 *Grãos de pedregulho retidos na peneira de abertura 4,8 mm - Determinação da massa específica, da massa específica aparente e da absorção de água [Grains of gravel retained in the 4.8 mm aperture sieve – Determination of specific mass, apparent specific mass and water absorption]*. Brazilian Association of Technical Standards, Rio de Janeiro, Brazil (in Portuguese).

Adarme, O. F. H. 2018 *Obtenção de biogás a partir da co-digestão anaeróbia de resíduos do processo de produção de bioetanol de primeira e segunda geração [Obtaining Biogas From the Anaerobic Co-digestion of Waste From the First- and Second-Generation Bioethanol Production Process]. Doctorate*, Federal University of Ouro Preto, Brazil (in Portuguese).

Ahmaruzzaman, M. 2010 A review on the utilization of the fly ash. *Progress in Energy and Combustion Science* **36**, 327–363.

Almeida, M. L. B., Ayres, E., Libânio, M., Garamano, D. S., Ribeiro, C. C. & Oréfice, R. L. 2020 Bio-based polyurethane foams with enriched surfaces of petroleum catalyst residues as adsorbents of organic pollutants in aqueous solutions. *Journal of Polymer and the Environment* **12**, 1–12.

Araújo, A. S. 2018 *Comparação entre os padrões de potabilidade nacional e internacionais quanto à presença de agrotóxicos [Comparison Between National and International Potability Standards for the Presence of Pesticides]. 2018. Monograph (Water Resources Management Specialization)*. Federal University of Minas Gerais, Belo Horizonte, Brazil (in Portuguese).

Bae, J. W. & Kwon, W. S. 2020 Investigating the effects of fipronil on male fertility: insight into the mechanism of capacitation. *Reproductive Toxicology* **94**, 1–7.

Canilha, L., Chandel, A. K., Milessi, T. S. S., Antunes, F. A. F., Freitas, W. L. C., Felipe, M. G. A. & Silva, S. S. 2012 Bioconversion of sugarcane biomass into ethanol: an overview about composition, pretreatment methods, detoxification of hydrolysates, enzymatic saccharification and ethanol fermentation. *Journal of Biomedicine and Biotechnology* **12**, 1–15.

Conab – Companhia Nacional de Abastecimento 2017 *2016 Monitoramento da safra brasileira de cana-de-açúcar*. National Supply Company. *Monitoring the Brazilian sugarcane crop*. v. 3 –2016/17 N. 4, 82 p., Brasilia, Brazil (in Portuguese).

Dallarés, S., Dourado, P., Sanahuja, I., Solovyev, M., Gisbertf, E., Montemurro, N., Torreblanca, A., Blázquez, M. & Solé, M. 2020 Multibiomarker approach to fipronil exposure in the fish *Dicentrarchus labrax* under two temperature regimes. *Aquatic Toxicology* **219**, 1–12.

Ferreira, P. P. L., Braga, R. M., Teodoro, N. M. A., Melo, V. R. M., Melo, D. M. A. & Melo, M. A. F. 2015 Adsorção de Cu $^{2+}$ e Cr $^{3+}$ em efluentes líquidos utilizando a cinza do bagaço da cana-de-açúcar [Adsorption of Cu^{2+} and Cr^{3+} in liquid effluents using sugarcane bagasse ash]. *Cerâmica* **61**, 435–441 (in Portuguese).

Gomes, H. O., Freire, P. T., Nascimento, R. F. & Teixeira, R. N. P. 2022 Removal of contaminants from water using *Moringa oleifera* Lam. as biosorbent: an overview of the last decade. *Journal of Water Process Engineering* **46**, 102576.

Kumari, U., Banerjee, T. & Singh, N. 2021 Evaluating ash and biochar mixed biomixtures for atrazine and fipronil degradation. *Environmental Technology & Innovation – Journals* **23**, 1–14.

Libânio, M. 2016 *Adsorção: Fundamentos de Qualidade e Tratamento de Água [Adsorption: Fundamentals of Water Quality and Treatment]*, 4th edn. Campinas, SP: Publishing Company Átomo. pp. 1–494 (in Portuguese).

Marchesan, E., Sartori, G. M. S., Avila, L. A., Machado, S. L. O., Zanella, R., Primel, E. G., Macedo, V. R. M. & Marchezan, M. G. 2010 Pesticides residues in the water of rivers of the Central Depression of the State of Rio Grande do Sul, Brazil. *Science Rural* **40**, 1053–1059.

Mor, S., Negi, P. & Ravindra, K. 2019 Potential of agro-waste sugarcane bagasse ash for the removal of ammoniacal nitrogen from landfill leachate. *Environmental Science and Pollution Research* **26**, 24516–24531.

Orlando, J. L., Smalling, K. L., Reilly, T. J., Fishman, N. S., Boehlke, A., Meyer, M. T. & Kivila, K. M. 2009 Occurrence of fungicides and other pesticides in surface water, groundwater, and sediment from three targeted-use areas in the United States. *U.S. Geological Survey Data Series* **797**, 73.

Regulation 888 2021 *Padrões de água potável, Ministério da Saúde*. Drinking Water Standards, Health Ministry, Brasília. p. 29 (in Portuguese).

Rodrigues, K. L. T., Sanson, A. L., Quaresma, A. V., Gomes, R. P., Silva, G. A. & Afonso, R. J. C. F. 2014 Chemometric approach to optimize the operational parameters of ESI for the determination of contaminants of emerging concern in aqueous matrices by LC-IT-TOF-HRMS. *Microchemical Journal* **117**, 242–249.

Rodríguez-Díaz, J. M., García, J. O. P., Sánchez, L. R. B., Silva, M. G. C., Silva, V. L. & Arteaga-Pérez, L. E. 2015 Comprehensive characterization of sugarcane bagasse ash for its use as an adsorbent. *BioEnergy Research* **8**, 1885–1895.

Rodríguez-Díaz, J. M., Andrade, C. A., Zambrano-Intriago, L. A., Sacon-Vera, E., Quiroz-Fernández, S., Silva, M. G. C. & Silva, V. L. 2021 Laboratory adsorption studies on Ni(II) and Zn(II) solutions by sugarcane-bagasse ash. *Water, Air, & Soil Pollution* **91**, 1–14.

Salomão, G. R., Américo-Pinheiro, J. H. P., Isique, W. D., Torres, N. H., Cruz, I. A. & Ferreira, L. F. R. 2019 Diclofenac removal in water supply by adsorption on composite low-cost material. *Environmental Technology* **1**, 1–17.

Sarker, T. C., Azam, S. M. G. G., El-Gawad, A. M. A. L., Gaglione, S. A. & Bonanomi, S. A. 2017 Sugarcane bagasse: a potential low-cost biosorbent for the removal of hazardous materials. *Clean Technologies and Environmental Policy* **19**, 2343–2362.

Shah, B., Tailor, R. & Shah, A. 2011 Adaptation of bagasse fly ash, a sugar industry solid waste into zeolitic material for the uptake of phenol. *Environmental Progress & Sustainable Energy* **30**, 358–367.

Tingle, C. C., Rother, J. A., Dewhurst, C. F., Lauer, S. & King, W. J. 2003 Fipronil: environmental fate, ecotoxicology, and human health concerns. *Reviews of Environmental Contamination and Toxicology* **176**, 1–66. 1st edition.

Toledo-Jaldin, H. P., Sánchez-Mendieta, V., Blanco-Flores, A., López-Téllez, G., Vilchis-Nestor, A. R. & Martín-Hernández, . 2019 Low-cost sugarcane bagasse and peanut shell magnetic composites applied in the removal of carbofuran and iprodione pesticides. *BioEnergy Research* **27**, 1885–1895.

USEPA – United States Environmental Protection Agency 1996 *Method 3050B: Acid Digestion of Sediments, Sludges, and Soils*. Washington, DC. *Revision 2*. Available from: https://www.epa.gov/sites/default/files/2015-06/documents/epa-3050b.pdf (accessed 22 June 2019).

USEPA – United States Environmental Protection Agency 2019 *Office of Prevention, Pesticides and Toxic Substances. New Pesticide Fact Sheet*. EPA-737-F-96-005, Washington, DC, 1996. Available from: http://fluoridealert.org/wp-content/pesticides/fipronil.epa.facts.may.1996.htm (accessed 20 June 2019).

Varsha, M., Kumar, P. S. & Rathic, S. 2022 A review on recent trends in the removal of emerging contaminants from aquatic environment using low-cost adsorbents. *Chemosphere* **287**, 132270.

Yadav, S. & Singh, N. 2020 Sugarcane trash ash: a low-cost adsorbent for atrazine and fipronil removal from water. *Indian Journal of Chemical Technology* **27**, 319–325.