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Research article

Batch adsorption of herbicides from aqueous solution onto diverse reusable materials and granulated activated carbon

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ABSTRACT

This study reports the kinetics and isotherms of the adsorption of five herbicides, MCPA, mecoprop-P, 2,4-D, fluroxypyr and triclopyr, from aqueous solutions onto a range of raw and pyrolysed waste materials originating from an industrial setting. The raw waste materials investigated demonstrated little capability for any herbicide adsorption. Granulated activated carbon (GAC) was capable of the best removal of the herbicides, with >95% removal observed. A first order kinetic model fitted the data best for GAC adsorption of 2,4-D, while a pseudo-first order model fitted the data best for GAC adsorption of fluroxypyr and triclopyr, indicating that adsorption was *via* physisorption. A pseudo-second order kinetic model fitted the GAC adsorption of MCPA and mecoprop-P, which is indicative of chemisorption. The adsorption of the herbicides in all cases was best described by the Freundlich model, indicating that adsorption occurred onto heterogeneous surfaces.

1. Introduction

A global population increase has necessitated an intensification of agricultural practices in order to achieve improved crop yields and production rates (Morillo and Villaverde, 2017). This has been accomplished, in part, by increased pesticide usage (Gavrilescu, 2005; Morillo and Villaverde, 2017; Khalid et al., 2020). Total annual pesticide sales in Europe during the period 2011 to 2016 rose by approximately 14% from 386,400 to 439,400 tonnes of active ingredients (Peña et al., 2020). In the United States, the use of the broad spectrum herbicide glyphosate has risen by approximately 19,700% from 635 tonnes in 1974 to 125,000 tonnes in 2014 (Zhang et al., 2019). While increased pesticide application has been beneficial in preventing hazardous diseases in crops, improving yields, and maintaining the economic viability of agriculture (Maggi et al., 2020), it has also increased the risk of subsequent human exposure, resulting in human health issues, such as neurological, respiratory and carcinogenic effects (Van Maele-Fabry et al., 2017; Ye et al., 2017; Pouchieu et al., 2018). It has also intensified the contact of these compounds with aquatic environments (Burri et al., 2019; Liu et al., 2019; Sahin and Karpuzcu, 2020). Mojiri et al. (2020) reported on pesticide concentrations in various aquatic environments across the world and found that pesticide levels ranged from 7 ng l^{-1} to 121222 ng l^{-1}, often well above the maximum allowable concentration of pesticides in drinking water (100 ng l^{-1}; Council of the European Union, 1998). As herbicides account for the biggest proportion of pesticide usage (Mojiri et al., 2020), their removal from aqueous environments is, therefore, an important scientific and environmental objective, according to the Food and Agriculture Organization of the United Nations (Food and Agricultural Organization of the United Nations).

Many media have been used as adsorbents for herbicides (Bayat et al., 2018; Papazlatani et al., 2019; Amoah-Antwi et al., 2020). Granulated activated carbon (GAC) is often used as an adsorbent for pesticides in Water Treatment Plants (Environmental Protection Agency / Health Service Executive, 2019), due to its large surface area (300–2500 m^2 g^{-1}) and highly microporous structure (Jusoh et al., 2011). Typical adsorption capacities for the herbicides MCPA and 2,4-D on GAC range from 174.2 mg g^{-1} to 181.8 mg g^{-1}, respectively (Ocampo-Pérez et al., 2012; Salman and Hameed, 2010). Biochar, a carbon-rich, porous material, has been used as a soil amendment

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because of its ability to adsorb pesticides from soils (Khalid et al., 2020), as well as for removal of pollutants from aqueous environments (Zhang et al., 2020; Kamali et al., 2021; Rana et al., 2021). However, its potentially adverse effects on soil biota, physicochemical changes in soil and even the presence of toxic substances in the biochar itself, have raised concerns regarding the long-term safety of its application (Brtnicky et al., 2021; Xiang et al., 2021). An alternative option is the use of agricultural and industrial waste materials (Ahmad and Danish, 2018; Jing et al., 2021). Industrial activities generate waste products from both consumption and production; however, the utilisation of these by-products is seldom examined in the literature (Grace et al., 2015). One drawback with the usage of industrial by-products for pesticide removal from aquatic environments is the possibility of introducing potentially toxic metals into those environments (Grace et al., 2016). A recent review by Tran et al. (2017) highlights errors and inconsistencies in publications on adsorption studies of contaminants from aqueous solution, including the inaccurate use of technical terms, mistakes relating to the study of adsorption kinetics and isotherms, as well as issues with adsorption mechanisms.

The aim of this study was to examine the adsorption of five of the most commonly used herbicides in Ireland (Department of AgricultureFood and the Marine, 2017), namely MCPA, mecoprop-P, 2,4-D, fluroxypyr and triclopyr (see Fig. 1), from aqueous solutions onto a range of raw materials originating from an industrial setting and pyrolysed materials.

2. Materials and Methods

2.1. Chemicals and materials used

The chemicals used were of analytical grade and solutions were prepared using Milli-Q ultrapure water [18.3 mΩ Milli-Q Element system™, Merck Millipore, UK]. The herbicides and chemicals were purchased from Sigma-Aldrich and used without further purification, specifically: MCPA (4-chloro-2-methylphenoxyacetic acid, $C_9H_9ClO_3$, 200.62 g mol^{-1}), mecoprop-P (*R*-2-(4-chloro-2-methylphenoxy)propionic acid, $C_{10}H_{11}ClO_3$, 214.65 g mol^{-1}), 2,4-D (2,4-dichlorophenoxyacetic acid, $C_8H_6Cl_2O_3$, 221.04 g mol^{-1}), fluroxypyr (4-amino-3,5-dichloro-6-fluoro-2-pyridyloxyacetic acid, $C_7H_5Cl_2FN_2O_3$, 255.03 g mol^{-1}), and triclopyr (3,5,6-trichloro-2-pyridyloxyacetic acid, $C_7H_4Cl_3NO_3$, 256.47 g mol^{-1}). Solutions were prepared at a concentration of 100 mg l^{-1} for each herbicide in 0.01 M $CaCl_2$ in Milli-Q ultrapure water and were shaken for a minimum of 24 h.

Twelve different materials, identified as potential adsorbents, were selected based on criteria such as low cost, bulk availability and potential for local sourcing. These were GAC, peat fibre, bottom ash, fly ash, blast slag, Phoslock©, zeolite, water treatment plant alum sludge (modified to adjust the physical characteristics to facilitate hydraulic conductivity without affecting the chemical characteristics of the alum sludge), two spruce biochars (S-BC1 and S-BC2), and two herbal pomace biochars (HP-BC1 and HP-BC2). The production processes and characterisation of all four biochars have been previously described (SigginsAbram and Healy, 2020). All adsorbents were dried at 105 °C for 24 h, then crushed or cut to a particle size of 1–2 mm, and stored in airtight containers at room temperature.

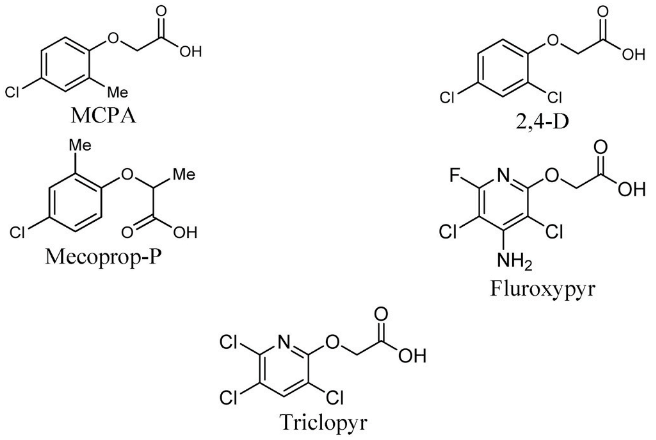

Fig. 1. Chemical structures of chosen herbicides.

2.2. Batch adsorption assays

An initial 72 h batch test adsorption assay was used to assess the abilities of each of the twelve materials to adsorb the selected herbicides. The results of these tests were used to identify the best performing adsorbents for further investigation. All batch tests were set up in 40 ml amber glass vials, with 40 ml of equilibration solution (100 mg l^{-1}) and an adsorbent dose of 5 g l^{-1}. Vials were sealed with a PTFE-lined cap and equilibrated for up to 72 h at 10 °C on a mechanical reciprocal shaker at 160 rpm. Control vials containing no adsorbent were included to precisely calculate adsorption by each material and account for loss of herbicides by other means. Once equilibration was reached, samples were filtered through a PTFE syringe filter (0.45 μm) and analysed immediately.

2.2.1. Adsorption kinetics

The two highest performing adsorbents from the 72 h batch study were assessed for the rate at which they adsorb herbicides, using a kinetic study. Replicate vials for each material were sampled at times of 0, 1, 2, 3, 4, 6, 16, 18, 20 and 24 h. The values for time point zero were determined by adding a herbicide solution to the adsorbent in vials, and to an adsorbent-free control vial, followed by immediate filtration and analysis. The data were fitted to the linear version of first and second order (Ahmad et al., 2013), pseudo-first (Lagergren, 1898) and pseudo-second order (Ho and McKay, 1999), Elovich (Roginsky and Zeldovich, 1934) and intraparticle diffusion (McKay and Poots, 1980) kinetic equations to see which kinetic equations modelled the kinetic data the best (Table S1). The goodness of fit of all models was assessed by calculating the coefficient of determination (r^2; Eq. (1)) and the non-linear models were also assessed by calculation of the chi-squared value (χ^2; Eq. (2)). High r^2 and low χ^2 values are indicative that the data are a good fit to the model.

$$r2 = 1 - \frac{\sum (q_{\exp} - q_{calc})^2}{\sum (q_{\exp} - q_{\exp.mean})^2} \tag{1}$$

$$x^2 = \sum \frac{(q_{\exp} - q_{calc})^2}{q_{calc}} \tag{2}$$

where: q_{exp} is the experimental sorption capacity (mg.g^{-1}), q_{calc} is the modelled sorption capacity (mg.g^{-1}), and $q_{exp,\ mean}$ is the mean of the experimental sorption capacities.

The standard error of estimates (SEE; Eq. (3)) values was used to investigate the goodness of fit for the kinetic models. A high r^2 and low SEE are indicative that the data are a good fit to the model.

$$SEE = \sqrt{\frac{\left(\sum_{\exp} - \sum q_{calc}\right)^2}{(n-2)}} \tag{3}$$

where: q_{exp} is the experimental sorption capacity (mg.g^{-1}), q_{calc} is the modelled sorption capacity (mg.g^{-1}), and $q_{exp,\ mean}$ is the mean of the experimental sorption capacities.

2.2.2. Adsorption isotherms

Once an optimum time was identified from the kinetics experiments, an adsorption isotherm test was conducted for the media. The adsorption capability of the selected media were assessed across an adsorbent range of 0.25–5 g l^{-1}, using a herbicide solution at a herbicide concentration of 100 mg l^{-1} for 72 h. Experimental data were modelled by linear and non-linear Langmuir (1916), Freundlich (1906), Koble-Corrigan (Koble and Corrigan, 1952), Temkin (Vijayaraghavan et al., 2006) and Dubinin-Radushkevich (Vijayaraghavan et al., 2006) adsorption isotherms, using MS Excel's Solver plugin to determine the best fitting parameters by maximising for r^2 for the non-linear models.

2.3. Effect of pH on adsorption

The impact of pH on the adsorption capabilities of the two best performing media was investigated. The herbicide solutions were prepared as described in Section 2.1. Each solution was then divided into three portions, each buffered with NaOH to a pH of either 5, 7, or 9. The pH range for all unbuffered herbicide solutions was 3–4. Batch assays were conducted over 24 h using 40 ml amber glass vials, with 40 ml of appropriate buffered solution (100 mg l^{-1}) and an adsorbent dose of 5 g l^{-1}.

2.4. Herbicide analysis

Herbicide concentrations in the filtered samples, for all herbicides, were directly quantified. Methods for the determination of pesticide adsorption are limited by the high cost of the mass spectrometry equipment required for their analyses, coupled with the time-consuming pre-treatment techniques (Huang et al., 2009; Wang et al., 2019). UV–Vis spectrometry, as an analytical technique for the detection of pesticides in solution, has been widely used for more than twenty years (Bekbölet et al., 1999; Spaltro et al., 2018; Rizzi et al., 2020) despite the poor sensitivity of the technique when compared to the low level detection (ng.l^{-1}) as provided by modern mass spectrometry techniques. All samples were analysed using a Varian CARY 50 UV–Vis–NIR spectrophotometer (Varian Inc., now Agilent Technologies Inc., Santa Clara, CA, USA). Quantification was measured at the appropriate wavelength for each herbicide: 571 nm (glyphosate), 278 nm (MCPA), 280 nm (mecoprop-P), 283 nm (2,4-D), 263 nm (fluroxypyr) and 295 nm (triclopyr) (Lewis et al., 2016). UV–Vis readings were compared to standard curves in a range of 10–100 mg l^{-1} for quantification of each herbicide.

The LOD (mg.l^{-1}) and LOQ (mg.l^{-1}) for each herbicide using UV–Vis spectroscopy were calculated and are shown in Table 1.

2.5. GAC characterisation

A Hitachi S4700 Scanning Electron Microscope (SEM) equipped with a Bruker X-Flash EDX detector was used to image the sample of GAC and to determine its elemental composition. Fourier Transform Infrared Spectroscopy (FTIR) spectra analysis was carried out to identify functional groups on the surface of GAC, with and without the adsorption of the herbicides, using a PerkinElmer Spectrum 400 fitted with an ATR reflectance attachment. Spectra were collected in the 4000 to 650 cm^{-1} range with a resolution of 4 cm^{-1} and twenty integrated scans on a diamond/ZnSe window.

Table 1
LOD and LOQ values for the chosen herbicides.

	LOD (mg.l^{-1})	LOQ (mg.l^{-1})
MCPA	0.76	2.55
Mecoprop-P	6.03	18.27
2,4-D	3.82	12.73
Glyphosate	4.51	15.03
Triclopyr	1.25	4.17
Fluroxypyr	3.00	9.98

3. Results and discussion

3.1. Media analysis

The chemical characterisation of the media used has been previously reported (Grace et al., 2015; SigginsAbram and Healy, 2020), with the exception of the modified water treatment plant sludge (Table 2).

3.2. Adsorbent screening

GAC performed the best for the adsorption of all herbicides (>95% removal; Fig. 2). The raw materials had limited adsorption of any of the herbicides.

Of the four biochars investigated, S-BC-2 performed best removing MCPA, triclopyr and fluroxypyr (Fig. 2). The pore diameter of the four biochars varied from 60 to 390 Å (SigginsAbram and Healy, 2020), which is sufficient to prevent size exclusion that occurs when the pore diameter is less than 1.7 times the second largest dimension of the target compounds (Kasaoka, 1987). Size exclusion occurs when dissolved molecules of various sizes flow over a material containing pores, with the smaller molecules entering the pores but the larger ones being excluded. In the case of the herbicides examined in the current study, adsorbent pore diameters of >17 Å should be sufficient to prevent size exclusion. The surface area for each of the twelve raw or processed waste materials was determined (Table 2) and showed that GAC had the largest surface area of all the media used in this study. The media with the second and third largest surface areas were HP-BC1 and HP-BC2 but neither of these demonstrated any adsorption of the herbicides used. Interestingly, S-BC2 has only a surface area of 39 m^2 g^{-1}, yet it is the second best media at the adsorption of the herbicides, suggesting that surface area alone is not the main factor in the adsorption process. MCPA, mecoprop-P, 2,4-D, triclopyr and fluroxypyr all contain an aromatic ring, either phenyl or pyridinyl in nature. This would suggest that π-π interactions between the aromatic rings of the herbicides and the surface of GAC promote the adsorption of these five herbicides. As herbicides are more complex molecules than simple metal ions, which adsorb using electrostatic chelation interactions as the main mechanistic pathway (Ma et al., 2015), the adsorption mechanisms will also be more complex. Further to the presence or absence of an aromatic ring, the adsorption mechanism of the selected herbicides will be dependent on the electron-donating abilities of the various functional groups attached to each herbicide, as well as the ionisability of any amine groups present. For all the herbicides, there are possible interactions available involving the carboxylate groups, the various halogen and amino groups present, as well as the nitrogen atom of the pyridine ring in the cases of triclopyr and fluroxypyr. Based on the adsorption data shown in Fig. 2, it was decided to use, for both the kinetic and isotherm studies, GAC for the adsorption of MCPA, mecoprop-P, 2,4-D, triclopyr and fluroxypyr.

3.3. GAC characterisation

The surface morphology of GAC is shown in Fig. S1. The surface of the GAC is not smooth but, instead, shows small clusters distributed over smooth platelets. No distinct pores were observed.

IR spectra were obtained of GAC samples that had been stirred in either water or the various herbicide solutions for 72 h (Fig. 3). The spectrum of GAC stirred in water showed a few minor shoulders at 1618 cm^{-1}, 1230 cm^{-1}, and 965 cm^{-1}, similar to that observed by SigginsAbram and Healy (2020), but with the addition of a water band at 3200 cm^{-1}, which is presumably due to surface water molecules. The spectra of GAC in all the herbicide solutions also showed the presence of this water peak. The differences between the spectra of GAC in water and of GAC in the various herbicide solutions are very subtle, as was expected (Fig. 3).

The spectra in Fig. 3 suggest that the adsorption of MCPA and mecoprop-P by GAC is by the same mechanism, as the IR values for GAC

Table 2
Chemical and physical characterisation of the chosen media.

Media Parameter	GAC[a]	Peat fibre	Bottom ash[a]	Fly ash[a]	Blast slag[a]	Phoslock	Zeolite[a]	MWTPS	S-BC1	S-BC2[b]	HP-BC1[b]	HP-BC2
Al (mg.kg^{-1})	49	217	n/d[c]	1223	2083	816	263	77405	821	n/d[c]	n/d[c]	n/d[c]
C (mg.kg^{-1})	n/d[c]	54.3	n/d[c]	n/d[c]	n/d[c]	7000	n/d[c]	13	42.9	n/d[c]	n/d[c]	n/d[c]
Ca (mg.kg^{-1})	n/d[c]	4133	n/d[c]	n/d[c]	n/d[c]	10100	n/d[c]	25367	55878	33000	39000	167000
Fe (mg.kg^{-1})	14	623	n/d[c]	189	90	331	23	3836	1375	3600	6100	11000
K (mg.kg^{-1})	n/d[c]	322	n/d[c]	n/d[c]	n/d[c]	2800	n/d[c]	86	53199	10000	26000	274000
Mg (mg.kg^{-1})	3.78	1082	2120	13.6	20.4	1400	12.8	190	11436	3300	6400	73000
P (mg.kg^{-1})	87	169	171	1044	4	2500	3	576	33482	2000	8900	96000
Moisture (%)	5	11.9	n/d[c]	n/d[c]	n/d[c]	9.9	n/d[c]	77	5.8	27	22.3	37.2
Org C (%)		97.8	n/d[c]	n/d[c]	n/d[c]	5.5	n/d[c]	n/d[c]	50.5	74.3	66.6	61.9
Pore diameter (Å)	61	I[d]	74	109	203	144	87	I[d]	137	390	60	60
Pore volume (cm^3.g^{-1})	0.496	I[d]	0.001	0.002	0.01	0.113	0.104	I[d]	0.033	0.03	0.001	0.03
Surface area (m^2.g^{-1})	579	0.003	1.80	1.779	2.49	35.72	38.67	I[d]	11.46	39	216	374

[a] Grace et al. (2015).
[b] SigginsAbram and Healy, 2020.
[c] n/d: not detected.
[d] Immeasurable.

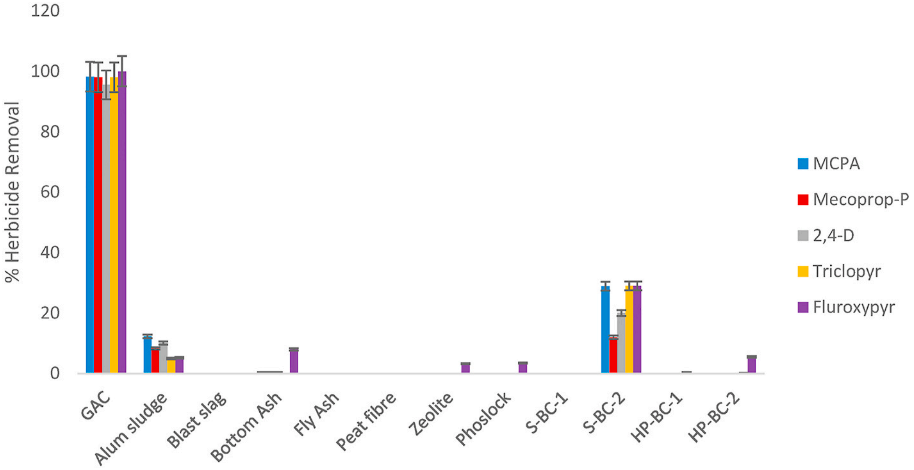

Fig. 2. Herbicide removal by twelve raw or processed waste materials at an adsorbent concentration of 5 g l^{-1} and herbicide concentrations of 100 mg l^{-1}, following equilibration for 72 h at 10 °C (±0.5 °C) and shaking at 160 rpm. Error bars represent standard error (stdev/$\sqrt{n}$, where n is the number of replicates, three in this case).

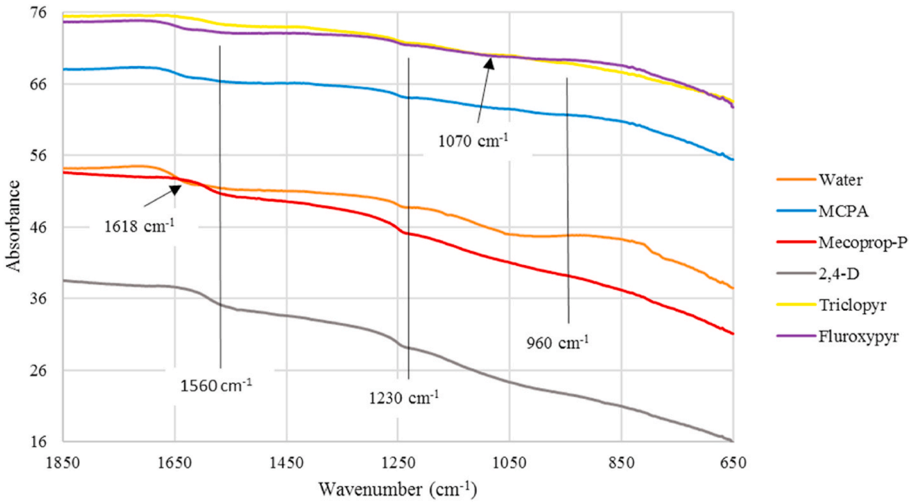

Fig. 3. FTIR spectra of GAC after being stirred in either water or one of the herbicide solutions for 72 h.

from both these solutions are similar, with the peak at 1618 cm^{-1} for GAC in water moving to 1555 cm^{-1} in both MCPA and mecoprop-P. This shift in peak position would suggest that a bonding interaction between the herbicide and GAC had occurred, which would imply that the mechanism of adsorption was by chemisorption. Similarly, the data also suggest that both triclopyr and fluroxypyr are adsorbed by GAC as again there are shifts in the peak at 1618 cm^{-1} to 1550 cm^{-1}. A new shoulder at 1068 cm^{-1} in both of these spectra indicates the presence of a pyridine ring which is involved in a binding interaction with the GAC, as this peak is normally at 1078 cm^{-1} for pyridine itself (Amudha et al., 2022). As this shift in peak position is only by a small number of wavenumbers, it would suggest that this binding interaction is by physisorption and not chemisorption. The FTIR spectrum of 2,4-D also shows a shift in the peak at 1618 cm^{-1} but, otherwise, very little information can be gathered from it. This may suggest that 2,4-D adsorbs by a different mechanism to either MCPA and mecoprop-P or triclopyr and fluroxypyr.

3.4. *Adsorption kinetics*

Adsorption kinetics were undertaken for each of the herbicides with their best adsorbent: GAC for MCPA, mecoprop-P, 2,4-D, triclopyr and fluroxypyr (Fig. 4). Maximum adsorption was reached for all herbicides adsorbed by GAC within 18 h of contact time (Fig. 4). Both MCPA and mecoprop-P demonstrated a two-phase adsorption characterised by a fast initial adsorption stage followed by a slower stage, as has been previously reported in kinetic adsorption studies (Ahmad et al., 2013).

The experimental kinetic data were fitted to a range of kinetic models (Table S1), and from these, the kinetic parameters were obtained (Table S2). Alberti et al. (2012) described adsorption as a sequential four step process: (1) transport of adsorbate to adsorbent, (2) diffusion of the adsorbate through the film layer surrounding the adsorbent, (3) intraparticle diffusion and (4) chemisorption. Fitting experimental data to kinetic models that have differing assumptions and evaluation of the fit, represented by high r^2 and low SEE values, allows the identification of the rate limiting step in the adsorption process.

These parameters indicate that the adsorption of both MCPA and mecoprop-P to GAC were pseudo-second order in nature, as a result of the high r^2 ($\geq$0.995) and low SEE ($\leq$0.004) values (Table S2). This indicates that chemisorption (step 4) is the rate-limiting step for these reactions and adsorption of these compounds occurs in a monolayer on the respective adsorbents' surface (Ahmad et al., 2013). This agrees with the IR spectra of GAC adsorption of both MCPA and mecoprop-P (Fig. 3), which suggested that both of these herbicides were adsorbed by a similar mechanism. This concurs with the kinetic results from previously reported studies for the adsorption of MCPA by activated carbon (Ocampo-Pérez et al., 2012; Pandiarajan et al., 2018). To the best of our knowledge, no kinetic adsorption studies of mecoprop-P using GAC as an adsorbent have been reported.

The adsorption of 2,4-D by GAC was best described by a first order kinetic model, as a result of the respective r^2 (0.989) and SEE (0.030) values (Table S2), which indicates that the transport of adsorbate to the adsorbent is the rate limiting step. The IR data (Fig. 3) suggested that 2,4-D was adsorbed by a different mechanism to both MCPA and mecoprop-P, even though a similar shift in the shoulder at 1618 cm^{-1} was observed in all three cases. This is in contrast to the reported studies (Pandiarajan et al., 2018; Bahrami et al., 2018; AmiriRoohi et al., 2020) where pseudo-first order and pseudo-second order kinetic models were documented, which would suggest that intraparticle diffusion and chemisorption were the rate limiting steps. In the current study, 12–20 mesh GAC was used, whereas 6–16 mesh GAC, Filtersorb 300 (F300) activated carbon, orange peel activated carbon, granulated activated carbon and canola-stalk-derived activated carbon, respectively, were used in the other studies (Aksu and Kabasakal, 2004; Salman and Hameed, 2010; Pandiarajan et al., 2018), which may have resulted in different rate limiting steps for the adsorption process.

In the current study, the kinetic adsorption of triclopyr and fluroxypyr by GAC fitted best to a pseudo-first order kinetic model (Table S2), which indicated that the rate limiting step was intraparticle diffusion (step 3). The IR spectra (Fig. 3) of GAC in both of these solutions showed an extra band in each spectrum at approximately 1074 and 1062 cm^{-1}, respectively. This band is due to the presence of a pyridine ring being present and involved in a bonding interaction with the GAC, as the IR band for pyridine itself is at 1078 cm^{-1} (Amudha et al., 2022). Pastrana-Martínez et al. (2010) reported on the adsorption of fluroxypyr onto different types of activated carbon and showed that a pseudo-second order kinetic model was the best fit for all types of the activated carbon chosen, which indicated that the rate limiting step was chemisorption. Again, the pore size of the various activated carbons in both studies could be one of the important factors in determining the overall kinetic model. To the best of our knowledge, no kinetic adsorption studies of triclopyr using GAC as adsorbent have been reported.

3.5. *Adsorption isotherms*

In order to get an insight into the adsorption capacity of the materials for herbicides, adsorption isotherm experiments were carried out (Fig. 5).

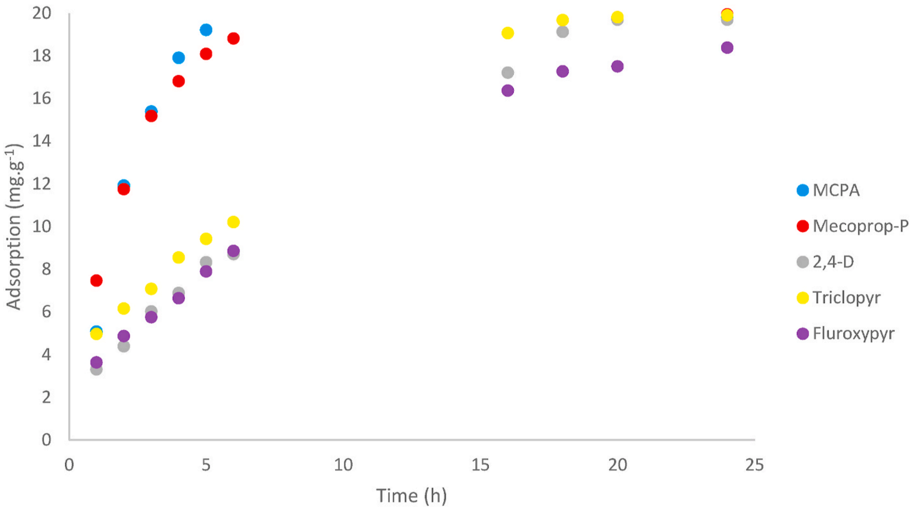

Fig. 4. Herbicide adsorption kinetics on GAC.

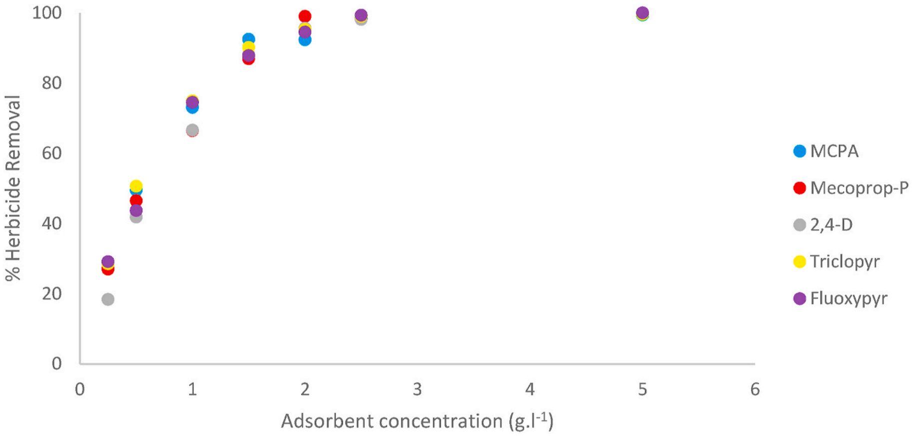

Fig. 5. Herbicide removal over a range of media concentrations, expressed as % herbicide removal. The adsorption study was carried out at a herbicide concentration of 100 mg l^{-1} and an equilibrium time of 72 h. Medium = GAC in all cases.

GAC removed >99% (19.9 mg g^{-1}) of all five target herbicides over 72 h at a concentration of 5 g l^{-1} (Fig. 3). All isotherms showed the L-type of Giles classification (Giles et al., 1974). For the adsorption of the various herbicides by GAC, this indicates that the aromatic rings of the herbicide molecules are adsorbed parallel to the carbon surface, as previously shown by Ocampo-Pérez et al. (2012). They also suggested that there was no competition for active adsorption sites on the carbon surface between the contaminant molecules and water molecules.

The various models, described in the Materials and Methods section, were applied in their linearised and non-linearised forms (Table S3), with Table S4 showing the isotherm parameters derived from each model. In all cases, based on the obtained r^2 values, the adsorption of all herbicides were best described by the Freundlich model (Fig. 6), which indicates that adsorption occurred as mono- and multi-layer adsorption on a heterogeneous surface. This involves both physisorption and chemisorption, which is in agreement with the pseudo-second order kinetic model obtained for both MCPA and mecoprop-P (Lin et al., 2015; Rizzi et al., 2019, 2020). Furthermore, an adsorption strength value of n which lies between 1 and 10 indicates that adsorption is favourable, as in the case of the herbicides, MCPA, mecoprop-P, 2,4-D, fluroxypyr and triclopyr (Table S4).

3.6. *Effect of pH*

The pH of an aqueous solution is one of the most significant parameters that influences the adsorption process, as it affects both the surface charge and the speciation of the target compound (Tan et al., 2015). No significant change in the adsorption of any of the herbicides, after 24 h, was detected at any pH studied compared to the adsorption observed when pH was not adjusted, indicated in the Figure by the caption MCPA 24 h (Fig. 7). The ability of corn cob biochar to adsorb 2, 4-D has been reported to have decreased dramatically in response to pH, from 95% at pH 2–5% at pH 12 (Binh and Nguyen, 2020). However, Essandoh et al. (2017) reported the effect of pH on the adsorption of both MCPA and 2,4-D onto switch grass biochar. They observed very little reduction in % removal of either MCPA or 2,4-D over a pH range of 2–8, with the % removal being reduced from 90% at pH 2–80% at pH 8. This lead them to suggest that, at naturally encountered pH values, switch grass biochar was a good adsorbent of MCPA and 2,4-D. It would appear that the influence of pH is dependent on the specific adsorbent, and that the adsorbents in our study were not affected.

4. Conclusions

The waste materials investigated demonstrated little capability for any herbicide adsorption. GAC was the best adsorbent observed for the removal of the herbicides investigated, with >95% removal. The data, supported by adsorption kinetic models and FTIR spectra, suggest that MCPA and mecoprop-P both fitted a pseudo-second order kinetic model, indicating that chemisorption was the rate limiting step. The experimental data also suggested that fluroxypyr and triclopyr fitted a pseudo-first order kinetic model, indicating that the rate limiting step was

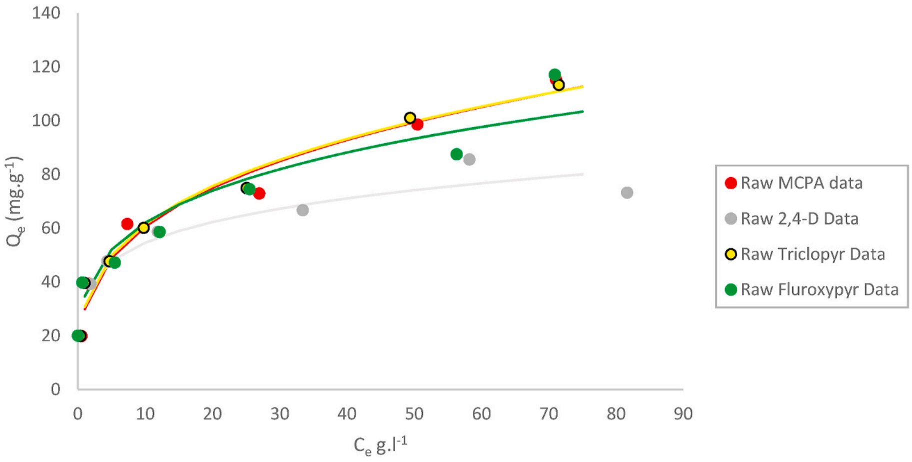

Fig. 6. Freundlich adsorption isotherm of MCPA, Mecoprop-P, 2,4-D, Triclopyr and Fluroxypyr on GAC. Modelled data are shown as a colour coded line. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

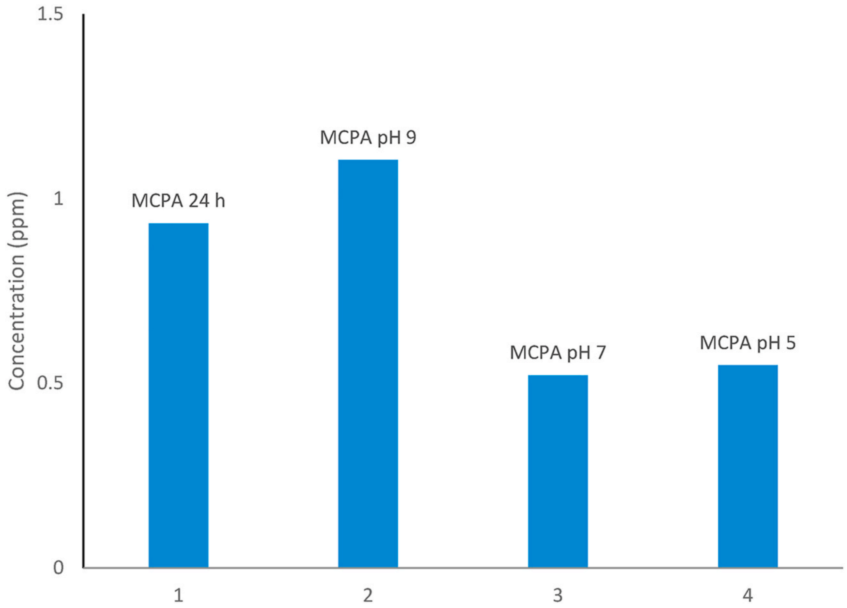

Fig. 7. Effect of pH on MCPA adsorption by GAC. MCPA = 100 ppm solution in ultrapure water, no pH adjustment; MCPA 24 h = MCPA solution after shaking with GAC (5 g l^{-1}) for 24 h, no pH adjustment; MCPA pH 9 = MCPA solution after shaking with GAC (5 g l^{-1}) for 24 h, pH 9; MCPA pH 7 = MCPA solution after shaking with GAC (5 g l^{-1}) for 24 h, pH 7; MCPA pH 5 = MCPA solution after shaking with GAC (5 g l^{-1}) for 24 h, pH 5.

intraparticle diffusion, while 2,4-D fitted a first order kinetic model, indicating that the transport of adsorbate to the adsorbent is the rate limiting step. The kinetic studies also indicated that the majority of the adsorption, in all cases, was completed within 18 h. The adsorption process followed the Freundlich isotherm model verifying monolayer and multilayer adsorption and in all cases the adsorption process was found to be favourable.

Author contributions

J. McGinley: Methodology; Investigation; Formal analysis; Writing – original draft; Writing – review and editing., M. G. Healy: Conceptualisation; Funding acquisition; Project administration; Supervision; Writing – review and editing. P. C. Ryan: Writing – review and editing. P.-E. Mellander: Writing – review and editing. L. Morrison: Writing – review and editing. J. Harmon O'Driscoll: Writing – review and editing. A. Siggins: Conceptualisation; Funding acquisition; Project administration; Supervision; Writing – review and editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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References

Ahmad, T., Danish, M., 2018. Prospects of banana waste utilization in wastewater treatment: a review. J. Environ. Manag. 206, 330–348.

Ahmad, M., Lee, S.S., Oh, S.E., Mohan, D., Moon, D.H., Lee, Y.H., Ok, Y.S., 2013. Modelling adsorption kinetics of trichloroethylene onto biochars derived from soybean stover and peanut shell wastes. Environ. Sci. Pollut. Res. 20, 8364–8373.

Aksu, Z., Kabasakal, E., 2004. Batch adsorption of 2,4-dichlorophenoxy-acetic acid (2,4-D) from aqueous solution by granular activated carbon. Separ. Purif. Technol. 35, 223–240.

Alberti, G., Amendola, V., Pesavento, M., Biesuz, R., 2012. Beyond the synthesis of novel solid phases: review on modelling of sorption phenomena. Coord. Chem. Rev. 256, 28–45.

Amiri, M.J., Roohi, R., Arshadi, M., Abbaspourrad, A., 2020. 2,4-D adsorption from agricultural subsurface drainage by canola stalk-derived activated carbon: insight into the adsorption kinetics models under batch and column conditions Environ. Sci. Pollut. Res. 27, 16983–16997.

Amoah-Antwi, C., Kwiatkowska-Malina, J., Thornton, S.F., Fenton, O., Malina, G., Szara, E., 2020. Restoration of soil quality using biochar and brown coal waste: a review. Sci. Total Environ. 722, 137852–137873.

Amudha, G., Santhakumari, R., R Chandrika, D., Mugeshini, S., Rajeswari, N., Sagadevan, S., 2022. Growth, spectroscopic and Hirshfeld surface analysis on pyridine urea single crystal. J. Mol. Struct. 1257, 132606–132614.

Bahrami, M., Amiri, M.J., Beigzadeh, B., 2018. Adsorption of 2,4-dichlorophenoxyacetic acid using rice husk biochar, granular activated carbon, and multi-walled carbon nanotubes in a fixed bed column system. Water Sci. Technol. 78, 1812–1821.

Bayat, M., Alighardashi, A., Sadeghasadi, A., 2018. Fixed-bed column and batch reactors performance in removal of diazinon pesticide from aqueous solutions by using walnut shell-modified activated carbon. Environ. Technol. Innovat. 12, 148–159.

Bekbölet, M., Yenigün, O., Yücel, I., 1999. Sorption studies of 2,4-D on selected soils. Water Air Soil Pollut. 111, 75–88.

Binh, Q.A., Nguyen, H.-H., 2020. Investigation the isotherm and kinetics of adsorption mechanism of herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) on corn cob biochar. Bioresource Technology Reports 11, 100520–100526.

Brtnicky, M., Datta, R., Holatko, J., Bielska, L., Gusiatin, Z.G., Kucerik, J., Hammerschmiedt, T., Danish, S., Radziemska, M., Mravcova, L., Fahad, S., Kintl, A., Sudoma, M., Ahmed, N., Pecina, V., 2021. A critical review of the possible adverse effects of biochar in the soil environment. Sci. Total Environ. 796, 148756–148773.

Burri, N.M., Weatherl, R., Moeck, C., Schirmer, M., 2019. A review of threats to groundwater quality in the anthropocene. Sci. Total Environ. 684, 136–154.

Council of the European Union, 1998. Drinking Water Directive 98/83/EC. Official Journal of the European Communities.

Department of Agriculture, Food and the Marine (DAFM), 2017. Pesticide Usage in Ireland, Grassland and Fodder Crops Survey Report.

Environmental Protection Agency/Health Service Executive (EPA/HSE), 2019. Pesticides in Drinking Water. Joint Position Paper.

Essandoh, M., Wolgemuth, D., Pittman Jr., C.U., Mohan, D., Mlsna, T., 2017. Phenoxy herbicide removal from aqueous solutions using fast pyrolysis switchgrass biochar. Chemosphere 174, 49–57.

Food and Agricultural Organization of the United Nations. Pesticide Use Database. http://www.fao.org/faostat/en/#data/RP._Food_and_Agriculture Organization. (Accessed September 2021).

Freundlich, H.M.F., 1906. Uber die adsorption in losungen. Z. Phys. Chem. 57, 385–470.

Gavrilescu, M., 2005. Fate of pesticides in the environment. Eng. Life Sci. 5, 497–526.

Giles, C.H., Smith, D., Huitson, A., 1974. A general treatment and classification of the solute adsorption isotherm. I. Theoretical. J. Colloid Interface Sci. 47, 755–765.

Grace, M.A., Healy, M.G., Clifford, E., 2015. Use of industrial by-products and natural media to adsorb nutrients, metals and organic carbon from drinking water. Sci. Total Environ. 518–519, 491–497.

Grace, M.A., Clifford, E., Healy, M.G., 2016. The potential for the use of waste products from a variety of sectors in water treatment processes. J. Clean. Prod. 137, 788–802.

Ho, Y.S., McKay, G., 1999. Pseudo-second order model for sorption processes. Process Biochem. 34, 451–465.

Huang, Z., Zhang, Y., Wang, L., Ding, L., Wang, M., Yan, H., Li, Y., Zhu, S., 2009. Simultaneous determination of 103 pesticide residues in tea samples by LC-MS/MS. J. Separ. Sci. 32, 1294–1301.

Jing, X., Li, Q., Qiao, X., Chen, J., Cai, X., 2021. Effects of accumulated straw residues on sorption of pesticides and antibiotics in soils with maize straw return. J. Hazard Mater. 418, 126213–126223.

Jusoh, A., Hartini, W.J.H., Ali, N., Endut, A., 2011. Study on the removal of pesticide in agricultural run off by granular activated carbon. Bioresour. Technol. 102, 5312–5318.

Kamali, M., Appels, L., Kwon, E.E., Aminabhavi, T.M., Dewil, R., 2021. Biochar in water and wastewater treatment - a sustainability assessment. Chem. Eng. J. 420, 129946–129966.

Kasaoka, S., 1987. Design of molecular sieving carbon-studies on adsorption of various dyes in liquid phase. Nippon Kagaku Kaishi 2260–2266, 1987.

Khalid, S., Shahid, M., Murtaza, B., Bibi, I., Natasha Naeem, M.A., Niazi, N.K., 2020. A critical review of different factors governing the fate of pesticides in soil under biochar application. Sci. Total Environ. 711, 134645–134662.

Koble, R.A., Corrigan, T.E., 1952. Adsorption isotherms for pure hydrocarbons. Ind. Eng. Chem. 44, 383–387.

Lagergren, S., 1898. About the theory of so-called adsorption of soluble substance. K. Sven. Vetersk. Handl. 24, 1–39.

Langmuir, I., 1916. Constitution and fundamental properties of solids and liquids. I. Solids. J. Am. Chem. Soc. 38, 2221–2295.

Lewis, K.A., Tzilivakis, J., Warner, D., Green, A., 2016. An international database for pesticide risk assessments and management. Hum. Ecol. Risk Assess. 22, 1050–1064.

Lin, K.-Y.A., Yang, H., Lee, W.-D., 2015. Enhanced removal of diclofenac from water using a zeolitic imidazole framework functionalized with cetyltrimethylammonium bromide (CTAB). RSC Adv. 5, 81330–81340.

Liu, T., Xu, S., Lu, S., Qin, P., Bi, B., Ding, H., Liu, Y., Guo, X., Liu, X., 2019. A review on removal of organophosphorus pesticides in constructed wetland: performance, mechanism and influencing factors. Sci. Total Environ. 651, 2247–2268.

Ma, X.F., Liu, X.Y., Anderson, D.P., Chang, P.R., 2015. Modification of porous starch for the adsorption of heavy metal ions from aqueous solution. Food Chem. 181, 133–139.

Maggi, F., la Cecilia, D., Tang, F.H.M., McBratney, A., 2020. The global environmental hazard of glyphosate use. Sci. Total Environ. 717, 137167–137178.

McKay, G., Poots, V.J., 1980. Kinetics and diffusion processes in colour removal from effluent using wood as an adsorbent. J. Chem. Technol. Biotechnol. 30, 279–292.

Mojiri, A., Zhou, J.L., Robinson, B., Ohashi, A., Ozaki, N., Kindaichi, T., Farraji, H., Vakili, M., 2020. Pesticides in aquatic environments and their removal by adsorption methods. Chemosphere 253, 126646–126669.

Morillo, E., Villaverde, J., 2017. Advanced technologies for the remediation of pesticide-contaminated soils. Sci. Total Environ. 586, 576–597.

Ocampo-Pérez, R., Abdel daiem, M.M., Rivera-Utrilla, J., Méndez-Díaz, J.D., Sánchez-Polo, M., 2012. Modeling adsorption rate of organic micropollutants present in landfill leachates onto granular activated carbon. J. Colloid Interface Sci. 385, 174–182.

Pandiarajan, A., Kamaraj, R., Vasudevan, S., Vasudevan, S., 2018. OPAC (orange peel activated carbon) derived from waste orange peel for the adsorption of chlorophenoxyacetic acid herbicides from water: adsorption isotherm, kinetic modelling and thermodynamic studies. Bioresour. Technol. 261, 329–341.

Papazlatani, C.V., Karas, P.A., Tucat, G., Karpouzas, D.G., 2019. Expanding the use of biobeds: degradation and adsorption of pesticides contained in effluents from seed-coating, bulb disinfestation and fruit-packaging activities. J. Environ. Manag. 248, 109221–109230.

Pastrana-Martínez, L.M., López-Ramón, M.V., Fontecha-Cámara, M.A., Moreno-Castilla, C., 2010. Batch and column adsorption of herbicide fluroxypyr on different types of activated carbons from water with varied degrees of hardness and alkalinity. Water Res. 44, 879–885.

Peña, A., Delgado-Moreno, L., Rodríguez-Liébana, J.A., 2020. A review of the impact of wastewater on the fate of pesticides in soils: effect of some soil and solution properties. Sci. Total Environ. 718, 134468–134488.

Pouchieu, C., Piel, C., Carles, C., Gruber, A., Helmer, C., Tual, S., Marcotullio, E., Lebailly, P., Baldi, I., 2018. Pesticide use in agriculture and Parkinson's disease in the AGRICAN cohort study. Int. J. Epidemiol. 47, 299–310.

Rana, A.K., Mishra, Y.K., Gupta, V.K., Thakur, V.K., 2021. Sustainable materials in the removal of pesticides from contaminated water: perspective on macro to nanoscale cellulose. Sci. Total Environ. 797, 149129–149152.

Rizzi, V., Romanazzi, F., Gubitosa, J., Fini, P., Romita, R., Agostiano, A., Petrella, A., Cosma, P., 2019. Chitosan film as eco-friendly and recyclable bio-adsorbent to remove/recover diclofenac, ketoprofen, and their mixture fromWastewater. Biomolecules 9, 571–592.

Rizzi, V., Gubitosa, J., Fini, P., Romita, R., Agostiano, A., Nuzzo, S., Cosma, P., 2020. Commercial bentonite clay as low-cost and recyclable "natural" adsorbent for the Carbendazim removal/recover from water: overview on the adsorption process and preliminary photodegradation considerations. Colloids Surf., A 602, 125060–125070.

Roginsky, S., Zeldovich, Y.B., 1934. The catalytic oxidation of carbon monoxide on manganese dioxide. Acta Phys. Chem. USSR 1, 554.

Sahin, C., Karpuzcu, M.E., 2020. Mitigation of organophosphate pesticide pollution in agricultural watersheds. Sci. Total Environ. 710, 136261–136268.

Salman, J.M., Hameed, B.H., 2010. Adsorption of 2,4-dichlorophenoxyacetic acid and carbofuran pesticides onto granular activated carbon. Desalination 256, 129–135.

Siggins, A., Abram, F., Healy, M.G., 2020. Pyrolysed waste materials show potential for remediation of trichloroethylene-contaminated water. J. Hazard Mater. 390, 121909–121917.

Spaltro, A., Pila, M., Simonetti, S., Álvarez-Torrellas, S., García Rodríguez, J., Ruiz, D., Díaz Compañy, A., Juan, A., Allegretti, P., 2018. Adsorption and removal of phenoxy acetic herbicides from water by using commercial activated carbons: experimental and computational studies. J. Contam. Hydrol. 218, 84–93.

Tan, X., Liu, Y., Zeng, G., Wang, X., Hu, X., Gu, Y., Yang, Z., 2015. Application of biochar for the removal of pollutants from aqueous solutions. Chemosphere 125, 70–85.

Tran, H.N., You, S.-J., Hosseini-Bandegharaei, A., Chao, H.-P., 2017. Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: a critical review. Water Res. 120, 88–116.

Van Maele-Fabry, G., Gamet-Payrastre, L., Lison, D., 2017. Residential exposure to pesticides as risk factor for childhood and young adult brain tumors: a systematic review and meta-analysis. Environ. Int. 106, 69–90.

Vijayaraghavan, K., Padmesh, T.V.N., Palanivelu, K., Velan, M., 2006. Biosorption of nickel(II) ions onto Sargassum wightii: application of two-parameter and three-parameter isotherm models. J. Hazard Mater. 133, 304–308.

Wang, X., Meng, X., Wu, Q., Wang, C., Wang, Z., 2019. Solid phase extraction of carbamate pesticides with porous organic polymer as adsorbent followed by high performance liquid chromatography-diode array detection. J. Chromatogr. A 1600, 9–16.

Xiang, L., Liu, S., Ye, S., Yang, H., Song, B., Qin, F., Shen, M., Tan, C., Zeng, G., Tan, X., 2021. Potential hazards of biochar: the negative environmental impacts of biochar applications. J. Hazard Mater. 420, 126611–126633.

Ye, M., Beach, J., Martin, J.W., Senthilselvan, A., 2017. Pesticide exposures and respiratory health in general populations. J. Environ. Sci. 51, 361–370.

Zhang, L., Rana, I., Shaffer, R.M., Taioli, E., Sheppard, L., 2019. Exposure to glyphosate-based herbicides and risk for non-Hodgkin lymphoma: a meta-analysis and supporting evidence. Mutat. Res. Rev. Mutat. Res. 781, 186–206.

Zhang, M., Song, G., Gelardi, D.L., Huang, L., Khan, E., Mašek, O., Parikh, S.J., Ok, Y.S., 2020. Evaluating biochar and its modifications for the removal of ammonium, nitrate, and phosphate in water. Water Res. 186, 116303–116312.