

Magnetic-Polypyrrole with Different Carbon Templates for Dispersive Separation of Endosulfan in Environmental Waters; A Comparative Study

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Two different carbon sorbents, graphene oxide (GO) and oil palm-based activated carbon (AC) were enhanced with magnetic polypyrrole (Mag-PPy) respectively to produce GO-Mag-PPy and AC-Mag-PPy. The synthesized sorbents were tested and compared based on the adsorption behaviour for micro-dispersive separation of endosulfan (ESO) in environmental waters using a gas chromatography microelectron captured detector (GC- μ ECD). Based on the extraction, the limit of detection (LOD) in decreasing order is GO-Mag-PPy > AC-Mag-PPy > Mag-PPy. This is expected, as the surface areas of the sorbents were dependent on the base sorbent used in the field emission scanning electron microscope (FESEM). When comparing GO-Mag-PPy and AC-Mag-PPy adsorption rates to their precursors, Mag-PPy, the sorbents with PPy addition were able to adsorb ESO more rapidly compared to its precursors. The rate of GO-Mag-PPy ($0.50 \text{ mg g}^{-1} \text{ min}^{-1}$) was 30% higher than AC-Mag-PPy ($0.23 \text{ mg g}^{-1} \text{ min}^{-1}$), followed by Mag-PPy ($0.19 \text{ mg g}^{-1} \text{ min}^{-1}$). From FESEM result, there is a difference in PPy coating on top of AC and GO, whereby GO was fully covered by PPy, while AC cavities were not thoroughly covered by PPy. This suggests different types of adsorptions occurring on the sorbent respectively. Adsorption capacities, represented by q_m at $C_e = 50 \text{ } \mu\text{g L}^{-1}$, in decreasing order were AC-Mag-PPy > GO-Mag-PPy > Mag-PPy. It is obvious that the addition of PPy only enhanced the adsorption capacity of sorbent to a certain extent. GO-Mag-PPy sorbent has the lowest LOD for the extraction of endosulfan. A reusability study found that AC-Mag-PPy is more robust compared to GO-Mag-PPy and Mag-PPy due to the physical shielding of magnetite and PPy in its cavities. It was concluded that the molecular structure of the base sorbent influenced the manner of the PPy and magnetite binding, and hence differ in the adsorption trends of ESO.

Keywords: Polypyrrole; MSPE; oil palm activated carbon; graphene; endosulfan

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Magnetic dispersive solid phase extraction (MSPE) has recently been considered one of the alternative preconcentration techniques for the extraction of different polar analytes in environmental waters (Hagarova 2020). MSPE allows more contact between the analyte and sorbents phase, reduction of sample treatment time, requires low solvent consumption, and overall easy handling in comparison with the traditional techniques (Islas *et al.*, 2017, Rashidi Nodeh *et al.*, 2016, Musa *et al.* 2018). One of the crucial steps in MSPE is the selection of sorbent, and it is necessary to consider chemical and physical characteristics that allow maximal extraction performance.

The main disadvantage of MSPE is the separation between the sorbent and matrix, either by filtration or centrifugation, which increases extraction time and additional separation steps. Furthermore, the deterioration of the magnetic nanoparticles tends to agglomerate easily (Petcharoen & Sirivat, 2012).

To overcome these challenges, the inclusion of magnetic nanoparticles and polymer in sorbent is considered. The usage of a polymer as a co-sorbent allows the sorbent to have high mechanical strength for hardy usage in MSPE, such as ultrasonic- or vortex-assisted extraction. Moreover, the addition of magnetite provides easy separation of sorbent in the matrix via an external magnet. Our previous works on magnetic solid phase extraction and polypyrrole polymer (PPy) as a sorbent have proven to be a suitable pair in the removal of pharmaceuticals and organic pesticides (Marsin *et al.*, 2018, Marsin *et al.*, 2020, Musa *et al.*, 2018). However, the usage of PPy as the main sorbent for MSPE is downgraded by the small surface area of the polymer. Recent studies show that carbonaceous material has been used as part of the dispersive sorbent composition, chosen for its high surface area. The wide variety of carbon as sorbent has been extensively studied as a sorbent on its own, and in combination with others

with good efficiency. Graphene, being the smallest carbon structure in the nanoscale is often chosen for more trace-level extraction (Rashidi Nodeh *et al.*, 2016, Musa *et al.* 2018), while carbon derived from biomass also has been considered one of the green alternatives as carbon sorbents such as from oil palm (Khalid *et al.*, 2020), corn (Suteu *et al.*, 2011) or rice-husk (Palagama *et al.*, 2019). This work discusses the different chosen carbonaceous materials; biomass-derived activated carbon and graphene oxide, as part of the Mag-PPy sorbent, in terms of physical and chemical attributes of the sorbent towards the extraction of a polar organochlorine pesticide, and endosulfan in environmental waters.

MATERIALS AND METHODS

Chemicals

The sorbents were prepared based on previous studies. The graphene-based sorbent (GO) was prepared via Hummer's method with modification (Hummers Jr & Offeman, 1958, Nodeh *et al.*, 2018), and the biomass-derived-activated carbon (AC) was prepared from oil palm empty fruit bunches from Sitiawan, Perak using physicochemical oxidation (Marsin *et al.*, 2020). The carbonaceous material was then combined with magnetite by co-precipitation method of aqueous $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ Sigma-Aldrich (St. Louis, USA) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ Sigma-Aldrich (St. Louis, USA) and later coated with PPy via chemical oxidative polymerization with FeCl_3 oxidant. All the chemicals used were analytical grade, and the analyte of interest, endosulfan used was CRM grade from Sigma-Aldrich (St. Louis, USA). The solvent used for standard dilution, hexane was also from Merck (Darmstadt, Germany) of analytical grade.

Apparatus

For characterization of the synthesized sorbent, a JEOL JSM-6390LV Field Emission Scanning Electron Microscope (FESEM). The sorbent was characterized to the surface area at 77 K using a standard BET procedure N_2 adsorption using a Micromeritics 3Flex surface area analyzer (Atlanta, USA). The VSM analysis was performed using a Lake Shore VSM 7400 vibrating sample magnetometer (Ohio, USA) at an applied maximum field of 15,000 G at room

temperature. The instrument used for the detection of endosulfan is using gas chromatography equipped with a microelectron-captured detector (GC- μ ECD). While, chromatographic separations of endosulfan were performed using an Agilent 7890A GC- μ ECD equipped with an HP5 column (30 m length \times 250 μm ID \times 0.25 μm film thickness). Helium was used as carrier gas (1 mL min^{-1}) while nitrogen was used as make-up gas (30 mL min^{-1}). The injection port was set at 290 $^\circ\text{C}$ while the oven was temperature-programmed from 120 $^\circ\text{C}$ to 190 $^\circ\text{C}$ at 40 $^\circ\text{C min}^{-1}$, then to 285 $^\circ\text{C}$ at 30 $^\circ\text{C min}^{-1}$. The endosulfan was identified based on its retention time of 2.98 min. Quantitative analysis was performed using an external standard method.

MSPE Procedure

The extraction capability of all sorbents was determined using the MSPE procedure. Sorbent (10 mg) was placed in a 50-mL centrifuge tube along with 10 mL water sample spiked with endosulfan (ESO). The sample was vortexed at 900 rpm to aid the dispersion of the sorbent. At the end of the MSPE process, magnetic sorbent was collected using an external magnet placed on the outside wall of the glass tube (collection time 30 s) and the solution was discarded. The collected sorbent was washed with deionized water (2×1 mL) and hexane (200 μL) was used to desorb the analytes (ultrasonication-assisted for 5 min). the desorbed sorbent was magnetically separated from the solution using an external magnet applied to the side of the glass tube. The solution was removed using a syringe and analysed using gas chromatography-micro-electron capture detection (GC- μ ECD).

Adsorption Characteristics

To understand the characteristics of endosulfan adsorption process onto the sorbent, kinetics and isotherms studies were calculated based on the experimental data collected, C_e , for the respective sorbents using the equations depicted in Table 1. Adsorption study was conducted on AC-Mag-PPy, GO-Mag-PPy and its precursor, Mag-PPy with different concentrations of endosulfan ESO ranging from 0.025 mgL^{-1} to 0.500 mgL^{-1} and fixed extraction time of 1.5 min.

Table 1. Different isotherm and kinetic models used in this study.

Model	Kinetic		Isotherm	
	Pseudo-first order	Pseudo-second order	Langmuir	Freundlich
Equation	$\ln (q_e - q_t) = \ln q_e - k_1 t$	$\frac{1}{q_t} = \frac{1}{k^2 q_e^2} + \frac{1}{q_e} t$	$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{k_L + q_{max}}$	$\ln q_e = \frac{1}{n} \ln C_e + \ln k_F$
x	t	t	C_e	$\ln C_e$
y	$\ln (q_e - q_t)$	$\frac{t}{q_t}$	$\frac{C_e}{q_e}$	$\ln q_e$
Slope (m)	k_1	$\frac{1}{q_e}$	$\frac{1}{q_{max}}$	$\frac{1}{n}$
Intercept (c)	$\ln (q_e)$	$\frac{1}{k_2^2 q_e^2}$	$\frac{1}{b q_{max}}$	$\ln k_F$
Assumption	Nil	Nil	R_L =separation factor	n = heterogeneity
Reference	Ho and McKay (1999)	Ho and McKay (1999)	Patil & Shrivastava (2015)	Fytianos et al., (2000)

RESULTS AND DISCUSSION

Physical Sorbent Attributes

For comparative studies, the sorbents following their optimum conditions and procedure were presented in Table 2. The sorbents were compared based on their physical attributes obtained in FESEM analysis (Fig. 1). The micrograph showed a different distribution of PPy and magnetite on different sets of sorbents (Fig. 1 A-C). The obvious difference is in the diameter of the PPy agglomeration, whereby the addition of carbon sorbent made the PPy diameter smaller from an average of 200 nm in Mag-PPy, to 170 nm in AC-Mag-PPy and 80 nm in GO-Mag-PPy. This is probably due to the template-polymerization of PPy

that occurred on top of the sorbent. The addition of carbon sorbent guided the chemical polymerization to match the carbon. The magnetite precipitated in between AC-Mag-PPy cavities and in between GO-Mag-PPy sheets, concealing the magnetite from disconnecting from its PPy sorbent. The largest particle size is from the synthesized biomass-activated carbon at a range of 157-300 nm. From VSM analysis in Figure 2 showed the curve for all magnetites in respective sorbents are paramagnetic. Interestingly, The magnetization strength of the sorbent in decreasing order; was Mag-PPy > AC-Mag-PPy > GO-Mag-PPy, This occurred because the magnetites were outweighed by the carbon added in the sorbent combination, thus reducing the magnetization strength.

Table 2. Physical attributes of (A) Mag-PPy, (B) AC-Mag-PPy and (C) GO-Mag-PPy.

Data of merit	Mag-PPy	AC-Mag-PPy	GO-Mag-PPy
Particle size (nm)	130-200 nm	157-300 nm	50 nm – 170 nm
Surface area (m ² g ⁻¹)	8.5	18.2	45.2
Pore diameter (A)	65.2	80.1	102.9
Magnetic strength, (emu g ⁻¹)	27.4	16.2	15.2
Amount of sorbent for extraction (mg)	10	10	10

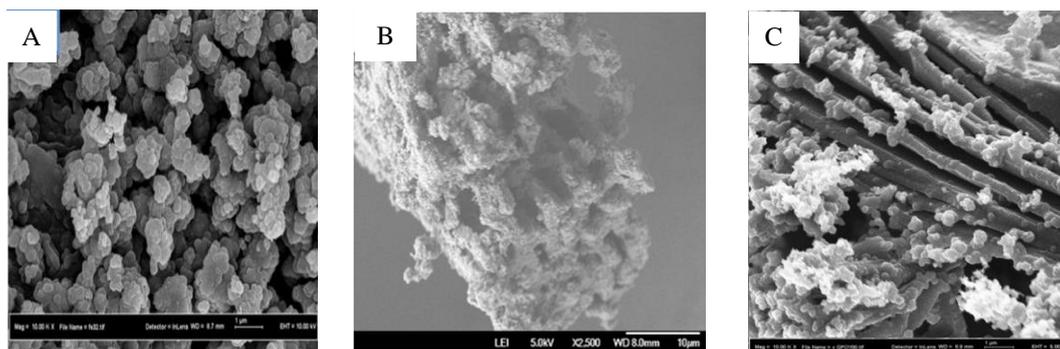


Figure 1. FESEM image of (A) Mag-PPy, (B) AC-Mag-PPy and (C) GO-Mag-PPy at 10,000 times magnification.

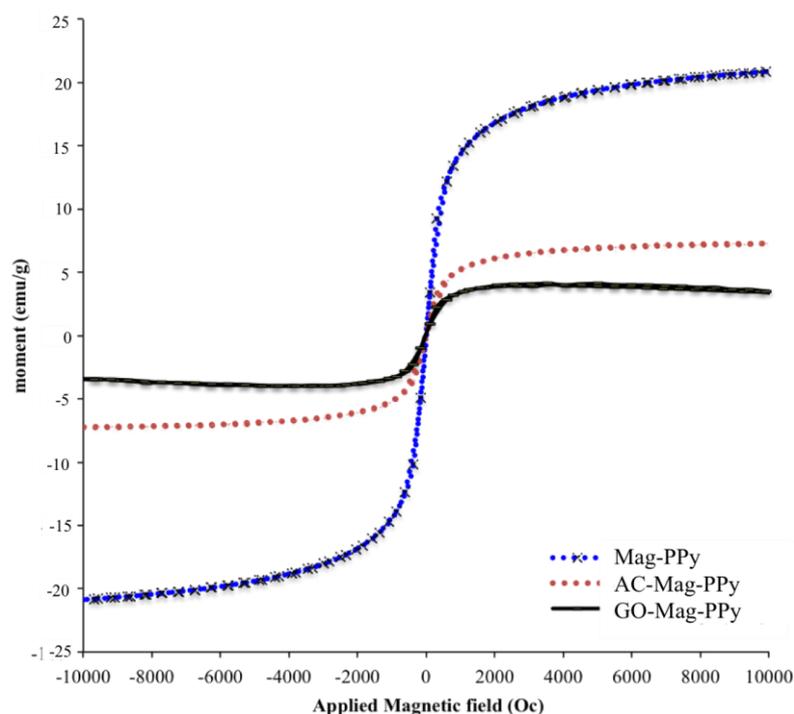


Figure 2. VSM analysis of (A) Mag-PPy, (B) AC-Mag-PPy and (C) GO-Mag-PPy.

Sorbent Extraction Performance

The sorbents following their optimum conditions and procedure were tabulated in Table 3. The precision, linearity, and accuracy of Mag-PPy, AC-Mag-PPy and GO-Mag-PPy were established using the AC-Mag-PPy-MSPE optimum conditions. It is shown that GO-Mag-PPy exhibits a greater ability to extract endosulfan in comparison to other sorbents, with LOD in decreasing order is GO-Mag-PPy > OPAC-Mag-PPy > Mag-PPy. This is expected as the surface area of the sorbents was dependent on the base sorbent used. The precision ($n=6$) and accuracy performance were similar between the sorbents. Recoveries in local tap water were also in the range of 98.1-101.9 %.

The sorbents were tested and compared based

on the adsorption behaviour of endosulfan using the MSPE method. The obtained adsorption kinetics of the sorbents is quick. Therefore, the best way for comparing the sorbents is to take a relevant analysis time for preconcentration of analytes, which is 10 min. in general, based on regression analysis, R^2 values for pseudo-second order were higher than first-order kinetics, thus chosen as the main model. The adsorption rate, denoted by K_{P2} ($\text{g mg}^{-1}\text{min}^{-1}$) of the sorbents in decreasing order is GO-Mag-PPy > AC-Mag-PPy > Mag-PPy, which suggested the adsorption rate increases with surface area. This is in line with other works by (Marsh & Rodrigues 2007, Apul *et al.*, 2013) that the high rate of K_{P2} indicates high attribution of chemisorption, due to additional strong organic interaction between carbon sorbent and the aromatic part of endosulfan by π - π interaction.

Table 3. Extraction performance of (A) Mag-PPy, (B) AC-Mag-PPy and (C) GO-Mag-PPy.

Data of merit	Mag-PPy	AC-Mag-PPy	GO-Mag-PPy
LOD (mg L ⁻¹)	3	0.23	0.007
LOQ (mg L ⁻¹)	5	0.75	0.01
Linearity (mg L ⁻¹)	5-500	0.5-150	0.01-1.0
Endosulfan Concentration (mg L ⁻¹)	100	1	0.01
Precision (interday) (%)	5.2	8.3	8.8
Accuracy (%)	4.4	12.8	8.8
Endosulfan Concentration (mg L ⁻¹)	100	0.05	0.01
Recovery % (tap water)	100.7	101.9	98.1
Reusability (cycle)	2	6	3

Two isotherm models; Langmuir, and Freundlich, were used at an endosulfan concentration of 50 µg L⁻¹. All sorbents fitted both models with R² > 0.95. The adsorption capacities by the Langmuir model, represented by q_m at $C_e=50$ µg L⁻¹, in decreasing order were AC-Mag-PPy > GO-Mag-PPy > Mag-PPy, with 84.10 mg g⁻¹, 60.57 mg g⁻¹, 27.96 mg g⁻¹ respectively. In the Freundlich model, the n value indicated heterogeneity of the surface; a higher n value is indicative of a homogeneous surface with narrow adsorption site distribution (Carter *et al.*, 1995). AC-Mag-PPy ($n=1.26$) as compared to Mag-PPy ($n= 1.59$) saw a decrement in homogeneity by 20 %, suggesting that PPy did not cover entirely the AC-Mag as the particle size is large, thus leaving an opportunity for AC to contribute as an adsorption site. Different for GO-Mag-PPy seeing an increase in n value up to 52 % ($n= 2.10$), indicating the presence of a more homogeneous surface, probably PPy polymerize and coated the entire GO small particles.

The reusability of sorbent was subjected to washing with hexane twice and drying in an oven at 85 °C for at least 2 h before letting it cool to room temperature before use. The extraction was done using 50 µg L⁻¹ of endosulfan and was repeated until endosulfan recovery < 90 %. Huge differences were seen in the performance of sorbents, where AC-Mag-PPy manage to use up to 6 times before it deteriorates, compared to GO-Mag-PPy and Mag-PPy only manage 3 and 2 times respectively. This was probably due to differences in particle size, where AC-Mag-PPy is larger and easier to collect. The magnetite also is well hidden in AC-Mag-PPy cavities, increasing its recovery.

CONCLUSION

A comparison of performance in terms of physical attributes and extraction performance was carried out for the developed materials, Mag-PPy with carbonaceous material addition as co-sorbent, AC-Mag-PPy and GO-Mag-PPy, using ESO as targeted analyte for organochlorine pesticide. The physical attributes showcased template-polymerization of PPy onto the carbon sorbent and different distributions of magnetite precipitated in the AC cavities, and in between the sheets of GO. The extraction performance has proven that the surface area of the sorbents was dependent on the base sorbent used with GO-Mag-PPy sorbent has the lowest LOD (0.007 mgL⁻¹) for the extraction of endosulfan. A reusability study found that AC-Mag-PPy has more advantages compared to GO-Mag-PPy and Mag-PPy due to the physical shielding of magnetite and PPy in its cavities. The kinetic study suggested a more heterogeneous active surface area in AC-Mag-PPy than GO-Mag-PPy. This was attributed to better polymerization of PPy onto AC-Mag compared to GO-Mag. These findings suggested two possibilities: (1) the size and polarity of carbon-based sorbents determine the size and mode of PPy attachment onto the composite, and/or (2) there is a limitation in terms of polymer bonding during the polymerization of PPy onto carbon-based sorbents. The selection of carbon-based sorbent as a polymerization template played a vital role in the determination of PPy size. From the Langmuir model, the selectivity of the analyte, R_L , was all in favor of the sorbent as all values were in the range of $0 > R_L > 1$, ($R_L = 0.33, 0.51$ and 0.37 for Mag-PPy, AC-Mag-PPy and GO-Mag-PPy respectively) indicating all sorbents are suitable to be used in MSPE of endosulfan in environmental

waters. Thus, it was concluded that the molecular structure of the base sorbent influenced the manner of the PPy and magnetite binding, and hence differ in the adsorption trends of ESO. This proves that the combination of carbon-base sorbent with magnetite and PPy plays a major role to obtain a highly selective sorbent for different applications of extraction; for sensitive and green MSPE.

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