Synthesis of Magnetic Carbonised Banana Peel as a Versatile and Reusable Adsorbent for Water Purification

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Abstract:

Discharge of industrial effluents containing dyes, heavy metal ions and pesticides poses a serious threat to the environment but current methods such as adsorption by activated carbon are expensive. Banana peel is a widely available food waste that has potential to be used as a biosorbent for removal of pollutants. Carbonising banana peel enhances its adsorption capacity, while magnetising it renders the separation after adsorption simple and convenient via the use of a magnet. Magnetic carbonised banana peel (MCB) was prepared by dispersing 3g to 5g of carbonised banana peel into 15ml of aqueous iron salts. The effectiveness of various MCBs in removing toxic pollutants like brilliant green, lead(II) ions and atrazine were investigated. Results show that the percentage removal of the 3 pollutants by MCB was more than 95% and the maximum adsorption capacity of MCB derived from the Langmuir isotherm was comparable to commercial activated carbon for lead(II) ions but slightly lower than that of commercial activated carbon for brilliant green. The effectiveness of MCB in removing brilliant green and lead(II) ions did not drop significantly after progressive cycles of adsorption and desorption, unlike commercial activated carbon. More than 95% of MCB can be retrieved during the recovery process and reused, in contrast to commercial activated carbon where only about 60% could be retrieved. MCB shows great promise to be used as a low-cost, eco-friendly, versatile and reusable adsorbent for water purification.

1. Introduction

1.1. Literature Review

With a rapid growth of industries, water pollution becomes a pertinent issue in today's context. Pollution is associated with an estimated 9 million deaths a year, with water pollution contributing to 1.8 million deaths (Mayor, 2017).

One common pollutant which is commonly discharged into water bodies is dye. In the textile industry, up to 200,000 tonnes of these dyes are lost to effluents every year due to the inefficiency of the dyeing process (Ogugbue & Sawidis, 2011), presenting major environmental problems for developing countries like Bangladesh (Yardley, 2013). One example of dye is brilliant green (BG), a toxic cationic dye that is widely used in the textile industries (Chiou & Li, 2002). Discharge of BG into the hydrosphere has an adverse effect on humans, causing irritation to the gastrointestinal and respiratory tract, as well as symptoms such as nausea, vomiting and diarrhoea (Kumar & Barakat, 2013).

Another type of common water pollutant is heavy metal ions, such as lead(II) ions. Leakages of lead(II) ions into the water bodies generally occur as a result of corrosion of lead-containing plumbing systems and surface runoffs of lead-based materials like paints (Yeo et al., 2013). A recent example is the drinking water crisis that occurred in the post-industrial city of Flint in Michigan, US, which resulted in hundreds of people being poisoned by lead contaminated water (Campbell et al., 2016). Lead(II) ions are known to cause neurological diseases that impair basic mobility functions, growth defects and even death (Rosen, 1995).

Atrazine is one of the most commonly used herbicides in the United States and Australia and is frequently detected in ground, surface and drinking water, such as in the lower Mississippi river and its tributaries (Pereira & Rostad, 1990). Atrazine contamination has heightened public concern over its environmental impact, as it is an endocrine disruptor for mammals and aquatic life (Chen, 2009). Human exposure to atrazine has been linked to adverse health effects like breast and prostate cancer as well as infertility (Giwa et al., 2019), thus treatment of herbicide-containing water is of paramount importance.

Current methods of removing toxic dyes and pesticides include chemical coagulation, adsorption (Gecgel, Ozcan & Gurpinar, 2013) and advanced oxidation processes (Silva et al., 2013). Metal ions are removed by chemical precipitation, ion exchange and adsorption. Among these methods, adsorption by activated carbon is one of the most effective methods because of its efficiency, capacity and scalability for commercial usage (Mattson & Mark, 1971). However, synthesis of activated carbon requires high temperatures of up to 800°C (Sabio et al., 2004), leading to high energy and capital costs (Moreno-Castilla et al., 1995). Retrievability is inefficient as it requires filtration or flocculation in order to remove the adsorbent-contaminant complex from water (Yeo et al., 2013).

Banana peels have attracted attention as a widely available and inexpensive biological waste (Li et al., 2016) to be used as eco-friendly adsorbents for water purification. The number of bananas consumed annually in the world is more than 100 billion, making it the fourth most important food crop after wheat, rice and corn (Suparto & Lin, 2016). Banana peels present a high adsorption capacity for metals and organic compounds (Thirumavalavan et al., 2010), primarily due to the presence of the hydroxyl and carboxyl groups of the pectin (Albarelli, Rabelo, Santos, Beppu, & Meireles, 2011). Carbonisation of banana peel can potentially enhance its adsorption capacity (Ponou, 2016) while magnetisation (via magnetite coating) serves as an easier and faster way of removing the adsorbent-contaminant complex in place of filtration or flocculation. Although there have been studies on the use of magnetized adsorbents such as waste tea and pollen grains to remove dyes and metal ions (Yeo et al., 2013), to date, there have been no studies on the use of magnetic banana peel for water purification.

1.2. Objectives

- To synthesise magnetic carbonised banana peel (MCB) via co-precipitation.
- To evaluate the adsorption capacity of MCB on brilliant green, lead(II) ions and atrazine as compared to commercial activated carbon (AC).
- To investigate the reusability of MCB after progressive cycles of adsorption and desorption.

1.3. Hypotheses

- MCB can be successfully synthesised via co-precipitation.
- The adsorption capacity of MCB on the three pollutants will be comparable to commercial activated carbon (AC).
- MCB can be reused for at least 3 cycles of adsorption and desorption.

2. Materials and Methods

2.1. Materials

Iron(III) chloride hexahydrate ($FeCl_3.6H_2O$), iron(II) sulfate heptahydrate ($FeSO_4.7H_2O$), 25% (w/w) aqueous ammonia and lead(II) nitrate ($Pb(NO_3)_2$) were purchased from GCE Laboratory Chemicals. Commercial activated carbon was procured from Unichem. Brilliant green ($C_{27}H_{34}N_2O_4S$) and atrazine ($C_8H_{14}ClN_5$) were purchased from Sigma Aldrich. Banana peels were obtained from the fruit and beverage stall in the school canteen of Hwa Chong Institution.

2.2. Synthesis of Magnetic Carbonised Banana Peel (MCB)

Banana peels were washed with deionised water, dried, and crushed into smaller pieces. It was then carbonised in a furnace at 450°C for 40 min under atmospheric conditions, and ground with a mortar and pestle into powder form. 6.66g of iron(III) chloride hexahydrate and 13.39g of iron(II) sulfate heptahydrate were dissolved in 45 ml of deionised water. Subsequently, carbonised banana peel (3g, 3.5g, 4g, 4.5g and 5g) was mixed and stirred in 15 ml of the iron salt solution. 25 ml of 25% (w/w) aqueous ammonia was then added into the solution to induce co-precipitation of magnetite onto the carbonised banana peel. The mixture was stirred and left to stand for 30 minutes before being filtered using vacuum filtration. The residue was washed until neutral pH and dried in an oven until constant. The chemical reaction for the co-precipitation of magnetite is shown below:

$$Fe^{2+} (aq) + 2Fe^{3+} (aq) + 8OH^{-} (aq) \rightarrow Fe_3O_4 (s) + 4H_2O (l)$$

The magnetic carbonised banana peels were labelled according to the mass of carbonised banana peel used in the synthesis, as shown in Table 1.

Table 1: Sample ID of magnetic carbonised banana peel (MCB)

Sample ID	Mass of carbonised banana peel used in synthesis/g	Volume of iron salt solution used/ml
MCB (3g)	3.0	15
MCB (3.5g)	3.5	
MCB (4g)	4.0	
MCB (4.5g)	4.5	
MCB (5g)	5.0	

2.3. Batch Adsorption Studies of Magnetic Carbonised Banana Peel (MCB)

0.2g of the various MCBs mentioned in Table 1 was added to 20 ml of brilliant green solution (50 mg/L), lead(II) ion solution (50 mg/L) or atrazine solution (5 mg/L) and shaken on an orbital shaker at 150 rpm for 24 hours. The concentration of atrazine was lower than the other two pollutants as it has limited solubility in water. A magnet was used to separate the magnetic adsorbent and the supernatant was obtained. Final concentration of brilliant green and atrazine were analysed using a UV-VIS spectrophotometer (Shimadzu UV 1800) at 627 nm and 222 nm respectively while that of lead(II) ions was analysed using an Atomic Absorption Spectrophotometer (AA 6300 Shimadzu). Five replicates were conducted for each type of adsorbent on each pollutant. Pollutant solutions which do not contain any adsorbent served as the controls for the experiments. The adsorption studies were also conducted on commercial AC, carbonised banana and unmodified banana peel for comparison with MCB. Since these adsorbents are not magnetic, they were separated from the solution using a centrifuge, whereas MCB was separated from the solution using a magnet instead. The percentage of brilliant green, lead(II) ions and atrazine removed was calculated using the following formula:

$$Percentage\ removed = \frac{Initial\ concentration - Final\ concentration}{Initial\ concentration} \times 100\%$$

For each pollutant, the MCB that could remove the highest percentage of pollutant while retaining its ability to be magnetically separated from the solution was selected for the adsorption isotherm studies and the reusability tests.

2.4. Adsorption Isotherms

Adsorption isotherms were determined by introducing 0.2g of MCB, carbonised banana peel and commercial AC to brilliant green and lead(II) ion solutions of concentrations from 50 to 1800 mg/L. Equilibrium concentration data was fitted into Langmuir and Freundlich isotherms (Appendix A, Pages 14-17).

2.5. Investigating the Reusability of Magnetic Carbonised Banana Peel (MCB)

After each adsorption study, 100 ml of ethanol was added to the used adsorbent to desorb the dye. The mixture was left to stand for 24 hours and the adsorbent was separated and dried.

The regenerated adsorbent was tested on its ability to re-adsorb brilliant green. The same procedure was used for lead(II) ions, except that ethanol was replaced by deionised water.

3. Results and Discussions

3.1. Characterisation of Magnetic Carbonised Banana Peel (MCB)

3.1.1. By Scanning Electron Microscopy (SEM)

Figure 1 reveals that banana peel has a rough, uneven surface and becomes porous after carbonisation (Figure 2). Figure 3 shows that magnetite particles are spherical and are about 30nm in size. After magnetisation, a coating of magnetite particles can be seen blocking the pores on the surface of the carbonised banana peel (Figure 4). The SEM images of MCB prepared by other masses of carbonised banana peel are similar to that synthesised using 3g (Figure 4).

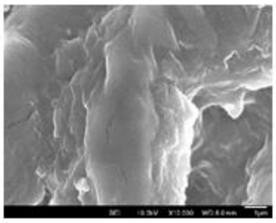

Figure 1: SEM image of banana peel

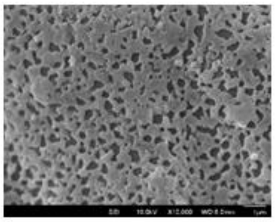

Figure 2: SEM image of carbonised banana peel

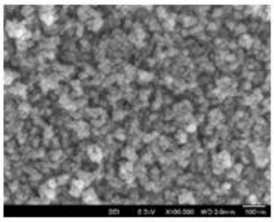

Figure 3: SEM of magnetite

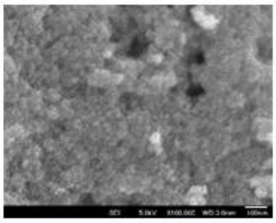

Figure 4: SEM image of MCB (3g)

3.1.2. By X-Ray Diffraction (XRD)

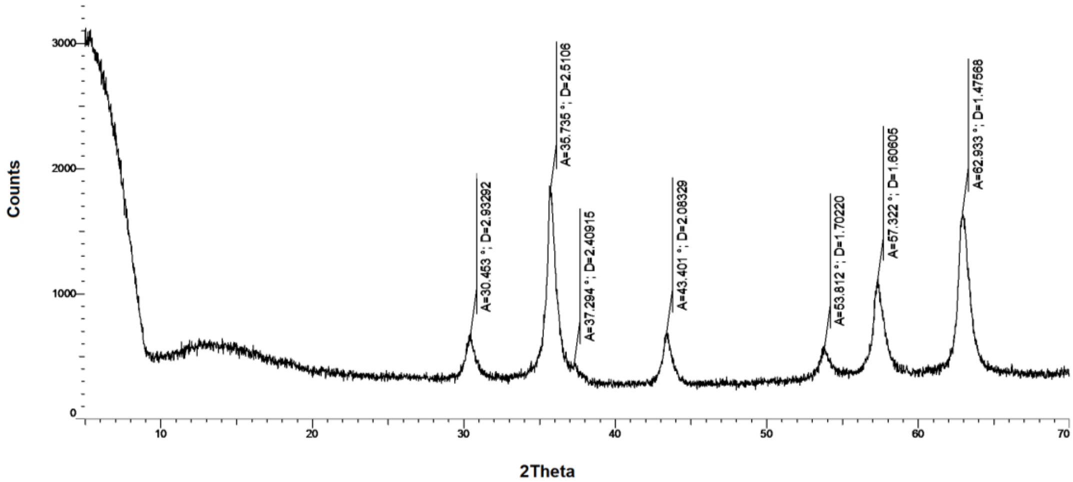

Figure 5: XRD spectrum of MCB (3g)

The XRD pattern of MCB (3g) (Figure 5) exhibits 2 theta peaks at 30.45°, 35.74°, 43.40°, 53.81°, 57.32°, 62.93° corresponding to crystal planes of (220), (311), (400), (422), (511) and (440) respectively, which is similar to that reported by Loh et al., (2008). This suggests that magnetite has been successfully coated onto the carbonised banana peel.

3.2. Batch Adsorption Studies of Magnetic Carbonised Banana Peel (MCB)

3.2.1. Atrazine

Figure 6 shows that commercial AC has the highest adsorption capacity, followed by carbonised banana peel and MCBs. The Kruskal-Wallis test on the results of various MCBs gives a p-value of 0.978 (>0.05), suggesting that there is no significant difference in the results of various MCBs. FTIR analysis (Figure 7) shows the presence of C=C stretching in aromatic rings in MCB, suggesting that atrazine is adsorbed via pi-pi interactions between the triazine ring in atrazine and the aromatic rings of carbon in MCB (Figure 8). The finding is in agreement with the study by Lupul, Yperman, Carleer and Gryglewicz (2014).

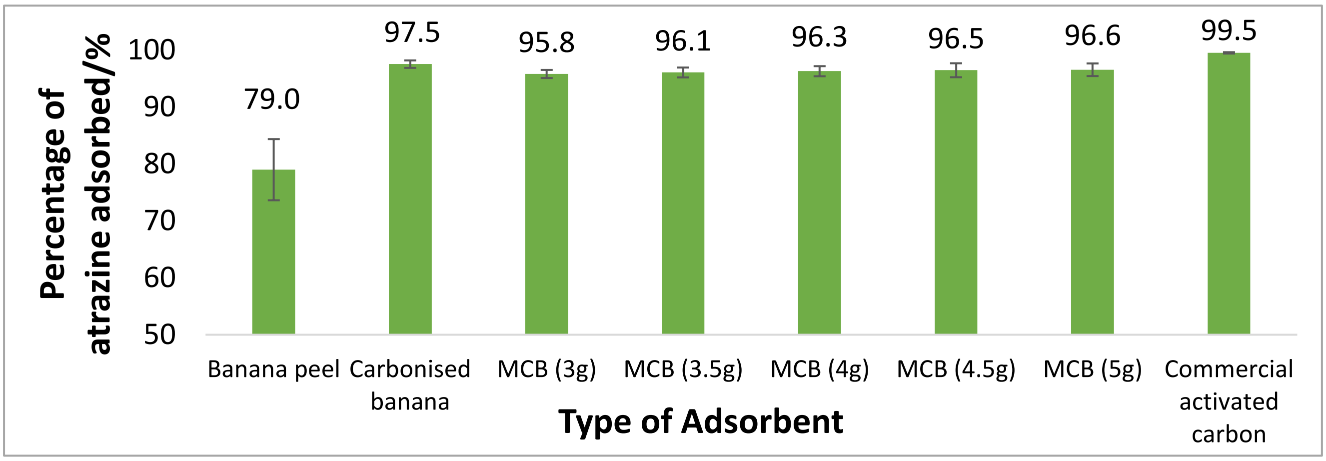

Figure 6: Adsorption of atrazine by different adsorbents. N=5

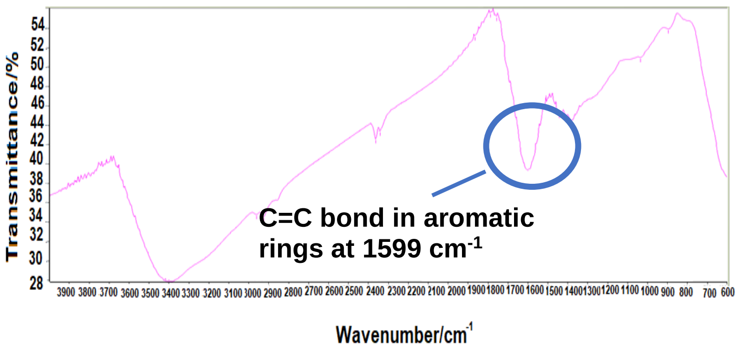

Figure 7: FTIR spectrum of MCB (3g)

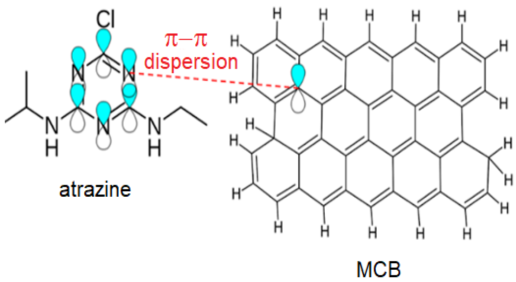

Figure 8: Proposed mechanism of how MCB adsorbs atrazine

3.2.2. Brilliant Green

Brilliant green is adsorbed via pi-pi interactions between aromatic rings of brilliant green and carbon (Calvete et al., 2010). Figure 9 shows that commercial AC has the highest adsorption capacity, followed by carbonised banana peel. This is likely due to the high porosity and surface area of both adsorbents (Figure 2). Comparing the percentage removal of MCB (3g) to MCB (5g) of brilliant green, it can be deduced that as the mass of carbonised banana peel added increases, the percentage removal of brilliant green increases (Figure 10). The Kruskal-Wallis test on the various MCBs in Figure 10 gives a p-value of 0.001 (<0.05), suggesting that there is a significant difference in the results of various MCBs. To explain the trend, acid digestion (Appendix B, Page 17) was carried out on various MCBs to determine the mass of magnetite coating per gram of MCB. Interestingly, as the mass of carbonised banana peel used during magnetisation increases, mass of magnetite coating on the carbonised banana peel decreases (Figure 11), and the percentage removal of brilliant green increases (Figure 10). This suggests that the presence of magnetite coating compromises adsorption capacity of MCB by blocking pores or binding sites in MCB, resulting in less area of contact between aromatic rings for adsorption. MCB (3.5g) was selected for subsequent tests on brilliant green as MCB (4g) to MCB (5g) were not as magnetic.

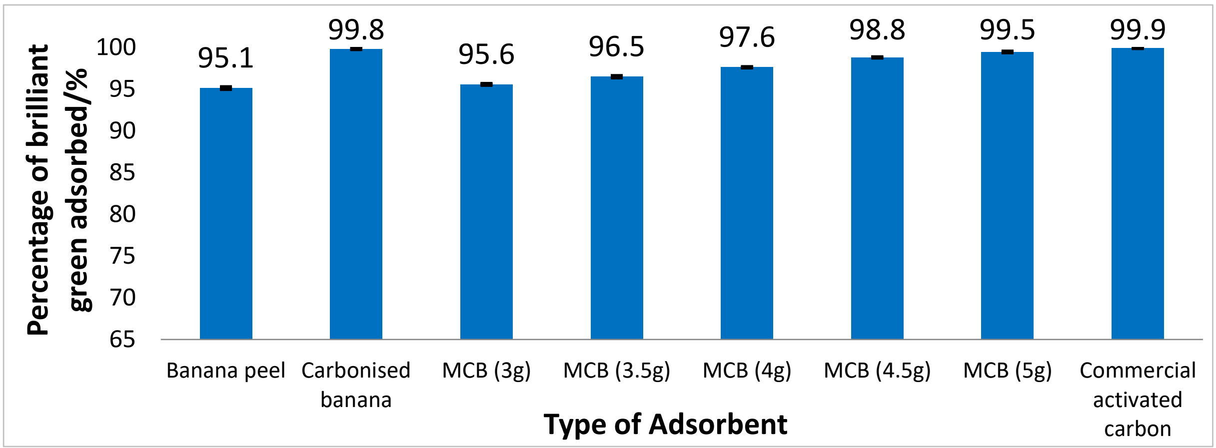

Figure 9: Adsorption of brilliant green by different adsorbents. N=5

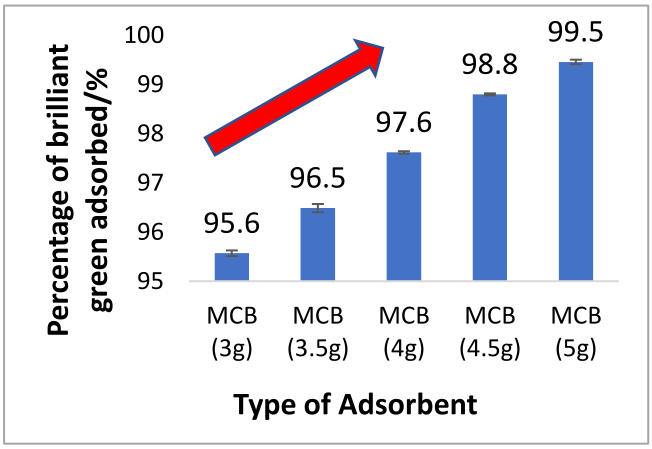

Figure 10: Adsorption of brilliant green by MCB (3g) to MCB (5g). N=5

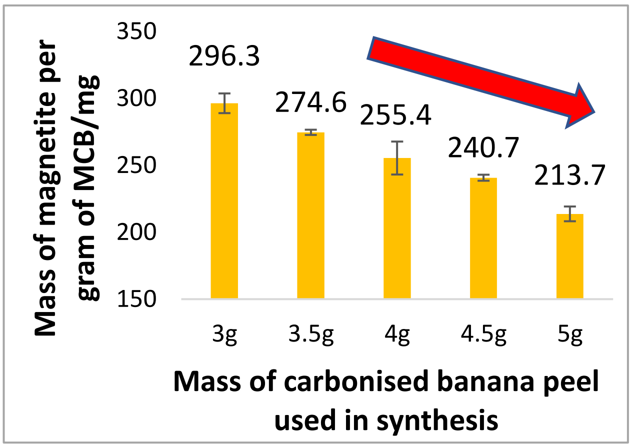

Figure 11: Mass of magnetite coating in MCB (3g) to MCB (5g). N=3

3.2.3. Lead(II) Ions

Figure 12 shows that MCB synthesised using various masses of carbonised banana peel all have close to 100% adsorption for lead(II) ions. Commercial AC has the next highest adsorption capacity, followed by carbonised banana peel, and lastly, banana peel.

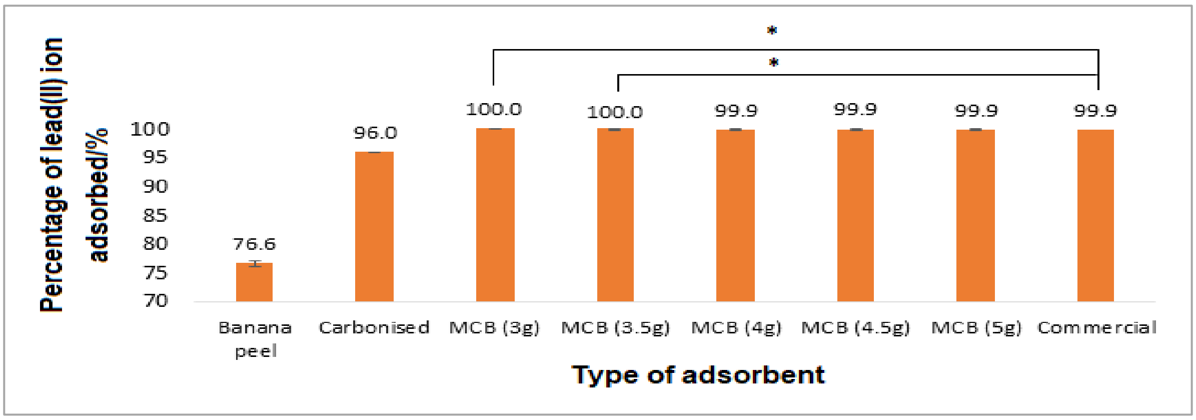

Figure 12: Adsorption of lead(II) ions by different adsorbents. * denotes significant difference based on Mann-Whitney U test at significance level of 0.05. N=5

There is a significant difference in the results of MCB (3g) and MCB (3.5g) when compared to AC (Figure 12). Energy Dispersive Spectroscopy (EDS) was then conducted to find out why.

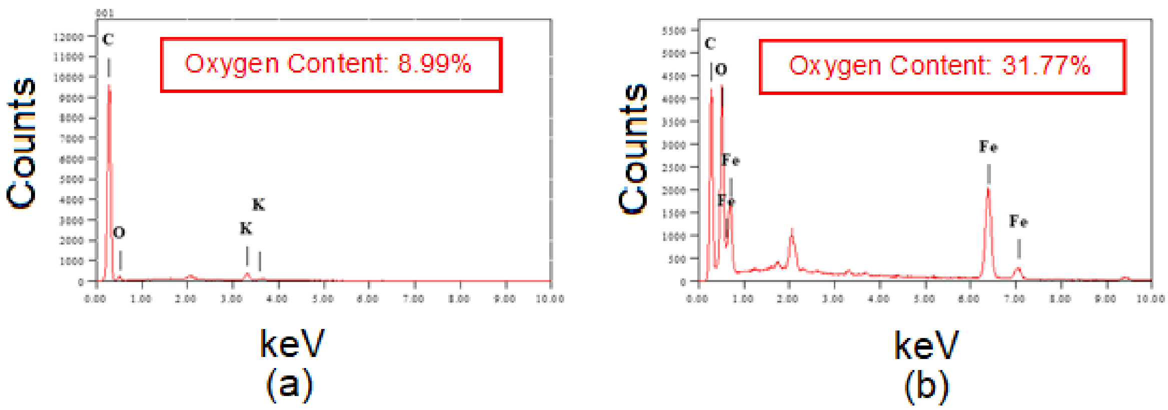

Figure 13: EDS of (a) Commercial AC and (b) MCB (3g)

Lead(II) ions are adsorbed via the formation of dative bonds between electron-deficient lead(II) ions and lone pairs of electrons (Huang et al., 2011). Figure 13 reveals that MCB has a greater oxygen content than AC, suggesting that there is more extensive dative bonding and hence, more effective adsorption of lead(II) ions in MCB. MCB (3g) was selected for future tests as it is most effective, requires the least carbonised banana peel for synthesis and yet magnetic.

3.3. Adsorption Isotherms

The equilibrium concentration data of MCB, carbonised banana peel and commercial AC were fitted into Langmuir and Freundlich isotherms (Appendix A, Pages 14-17). The Langmuir isotherm is a better fit for all 3 adsorbents, suggesting that the adsorption is monolayer. The maximum adsorption capacities of the 3 adsorbents were derived by taking the reciprocal of the gradient of equations obtained from Langmuir isotherms and the results were compared with adsorbents synthesised by other researchers (Tables 2 and 3).

For brilliant green, although MCB has a slightly lower maximum adsorption capacity than commercial AC and carbonised banana peel, its maximum adsorption capacity is higher than that of several eco-friendly adsorbents reported in literature (Table 2). For lead(II) ions, Table 3 shows that MCB has higher maximum adsorption capacity than both commercial AC and carbonised banana peel. MCB also outperforms various ACs synthesised by other researchers, suggesting that it has great potential to be used as adsorbents for water purification.

Table 2: Comparison of max. adsorption capacity of different adsorbents on brilliant green

Type of Adsorbent	Max. Adsorption Capacity/mg g^{-1}	Reference
Commercial AC	227	This study
Carbonised banana	196	This study
MCB	189	This study
Cactus fruit peel	143	Kumar & Barakat, 2013
ZnO-AC	143	Ghaedi et al., 2014
Chitosan beads	135	Ozkahraman et al., 2011

Table 3: Comparison of max. adsorption capacity of different adsorbents on lead(II) ions

Type of Adsorbent	Max. Adsorption Capacity/mg g^{-1}	Reference
MCB	41.3	This study
Commercial AC	39.2	This study
Carbonised banana	38.8	This study
Pine cone AC	27.5	Momcilovic et al., 2011
Coconut shell AC	26.5	Sekar et al., 2004
Eichhornia AC	16.6	Shekinah et al., 2002

3.4. Reusability of MCB

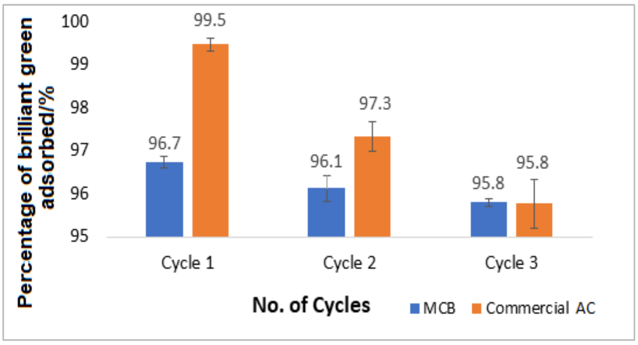

Figure 14: Regeneration of MCB and Commercial AC for re-adsorption of brilliant green. N=5

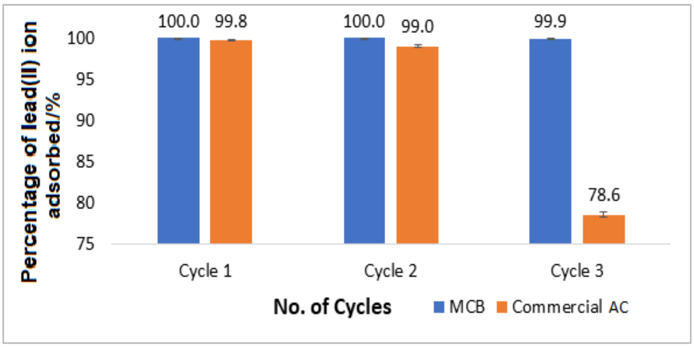

Figure 15: Regeneration of MCB and Commercial AC for re-adsorption of lead(II) ions. N=5

Figure 14 shows that after 3 cycles of adsorption of desorption, MCB is still able to effectively adsorb brilliant green, with the decrease in the percentage of dye removed being less than that of commercial AC. It is worth noting that in Cycle 3, there is no longer a significant difference in the results of AC and MCB (p-value of Mann-Whitney U test = 0.834 > 0.05). This suggests that the interaction between MCB and brilliant green is likely weak, thus allowing the dye to be easily desorbed.

For lead(II) ions, Figure 15 shows that MCB is able to adsorb lead(II) ions for 3 cycles of adsorption and desorption without a significant decrease in the percentage of lead(II) ions removed (p-value of Kruskal-Wallis test = 0.067 > 0.05). However, it can be seen that there is a significant drop (p-value of Mann-Whitney U test = 0.012 < 0.05) in percentage of lead(II) ions removed by AC in Cycle 3, suggesting that MCB has a greater potential than AC in adsorbing lead(II) ions in terms of reusability. Another advantage of MCB over AC is that as much as 97% of MCB could be retrieved after each cycle of adsorption, while only 60% of AC could be retrieved.

4. Conclusions and Future Work

Magnetic carbonised banana peel (MCB) was successfully synthesised via co-precipitation. MCBs were effective in removing brilliant green, atrazine and lead(II) ions, with the percentage removal being greater than 95%. Langmuir isotherm was a better fit for the adsorption of all 3 pollutants, suggesting that the adsorption by MCB is monolayer. Magnetising the carbonised banana peel lowers the maximum adsorption capacity on brilliant green slightly but enhances the maximum adsorption capacity of lead(II) ions. The magnetic property of MCB allows for a rapid, simple and convenient way of recovery by the use of a magnet, enabling it to be recycled effectively. MCB can be reused for at least 3 cycles of adsorption and desorption without a significant drop in effectiveness, saving cost and making the use of it in water treatment even more eco-friendly.

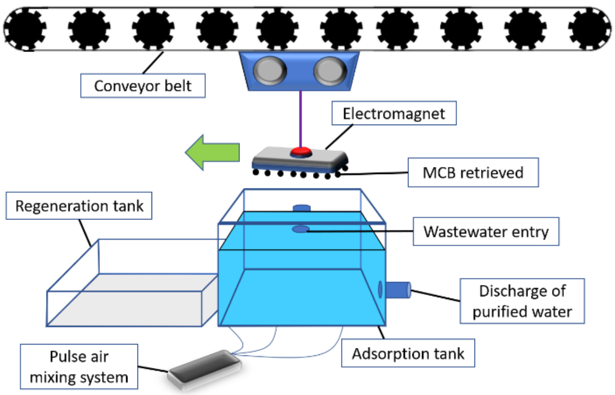

Figure 16: Proposed model for use of MCB in wastewater treatment plants

A model on how the MCB could be used in the industry was proposed (Figure 16). This model can be designed to be fully automated using robotics technology. After adsorption, a magnet will be used to attract the MCB from the adsorption tank and transport it to a regeneration tank where the MCB can be desorbed. Such a system facilitates the rapid and efficient retrieval of MCB, making the water purification process less time-consuming and more efficient.

In the future, the adsorption isotherm studies and reusability tests can be extended to atrazine. The effect of pH on the adsorption capacity of MCB can be studied, while thermodynamic studies and kinetic studies can also be conducted. MCB can also be applied in a real-life context to test its effectiveness in adsorbing pollutants from industrial wastewater and polluted water sources.

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Appendix A: Adsorption Isotherms of MCB, Carbonised Banana and Commercial AC

The equilibrium concentration data obtained from adsorption isotherm studies on brilliant green and lead(II) ions were fitted into the Langmuir isotherm and Freundlich isotherm.

The Langmuir isotherm assumes that adsorbed material is adsorbed over a uniform adsorbent surface at a constant temperature.

The linear form of Langmuir isotherm equation is given by:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}$$

Where C_e is the equilibrium concentration of adsorbate (mg/L), Q_e is the equilibrium capacity of the sorbents (mg/g), b is the Langmuir constant that indicates the sorption intensity and q_m is the maximum sorption capacity (mg/g).

The Freundlich isotherm assumes that the adsorption occurs on a heterogeneous surface.

The linear form of Freundlich equation is given by:

$$\log(qe) = \log(K_F) + \frac{1}{n}\log(C_e)$$

Where C_e is the equilibrium concentration of adsorbate (mg/L), Q_e is the equilibrium capacity of the sorbents (mg/g), K_F, a constant, is related to sorption capacity and n corresponds to sorption intensity.

The Langmuir and Freundlich isotherm plots for **brilliant green** are shown below:

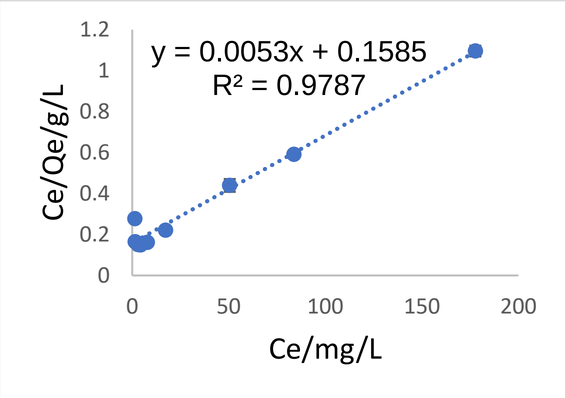

Figure 17: Langmuir isotherm for MCB

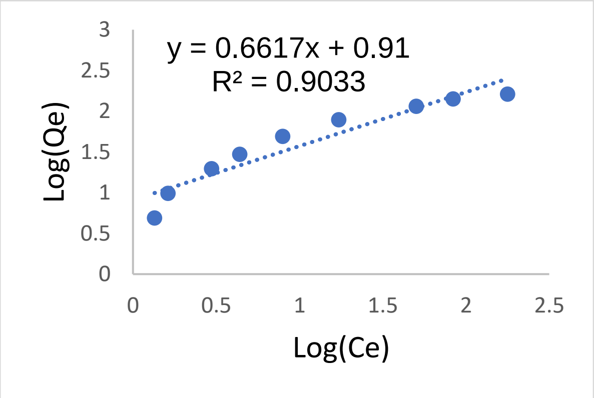

Figure 18: Freundlich isotherm for MCB

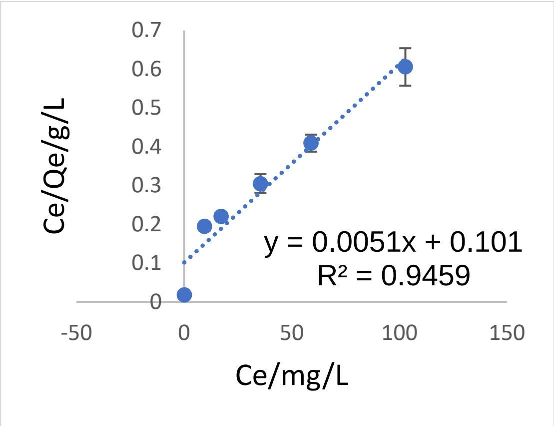

Figure 19: Langmuir isotherm for carbonised banana peel

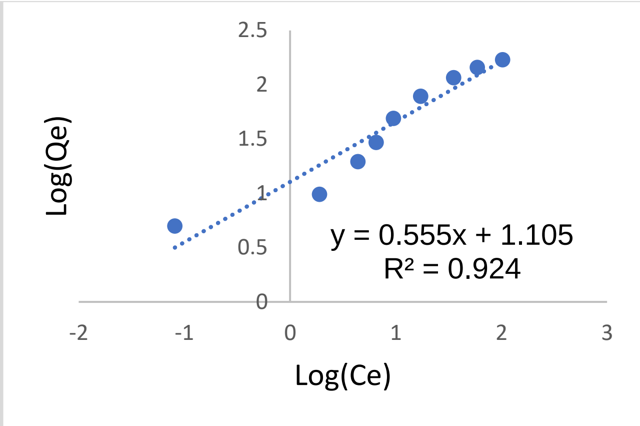

Figure 20: Freundlich isotherm for carbonised banana peel

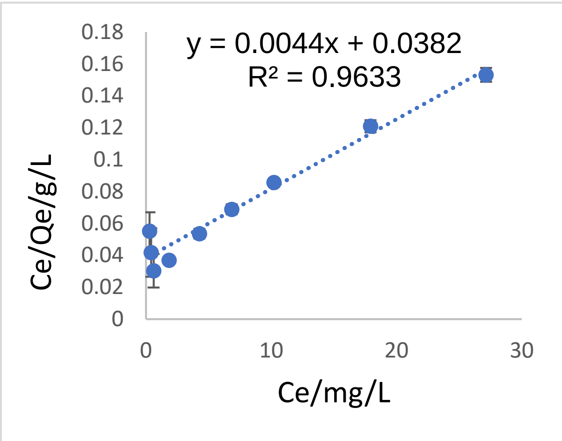

Figure 21: Langmuir isotherm for commercial AC

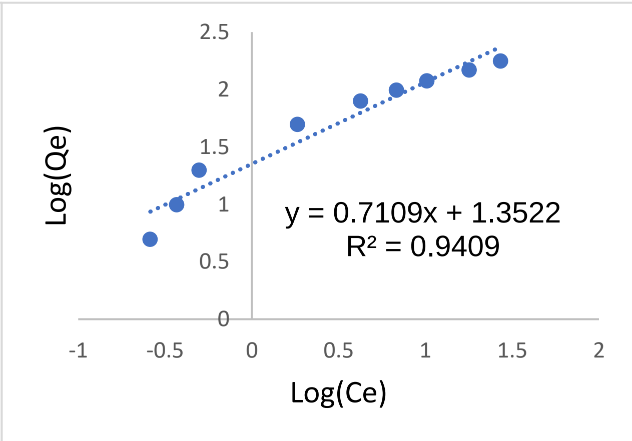

Figure 22: Freundlich isotherm for commercial AC

The values q_m (maximum adsorption capacity) were computed from the slope of Langmuir isotherm plots of C_e (mg/L) versus C_e/Q_e (g/L). Similarly, the values of n were computed from the slope of the Freundlich plot of $\log(Q_e)$ versus $\log(C_e)$.

The isotherm parameters obtained are summarised in table 4.

Table 4: Isotherm parameters for different adsorbents on brilliant green

	Langmuir Isotherm Parameters		**Freundlich Isotherm Parameters**	
Adsorbent	q_m (mg/g)	R^2	n	R^2
MCB	189	0.979	1.51	0.903
Carbonised Banana Peel	196	0.946	1.80	0.924
Commercial AC	227	0.963	1.41	0.941

Comparison of the coefficient of determination (R^2) of the linearized forms of both isotherms suggests that the Langmuir model yields a better fit for the equilibrium adsorption data of brilliant green onto MCB, carbonised banana peel and AC. The maximum adsorption capacity, q_m, of AC is the highest, followed by carbonised banana and MCB.

The Langmuir and Freundlich isotherm plots for **lead(II) ions** are shown below:

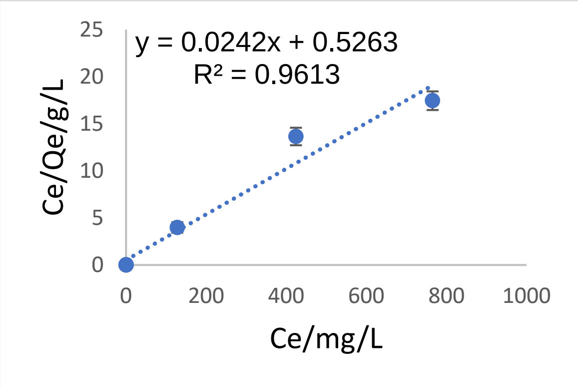

Figure 23: Langmuir isotherm for MCB

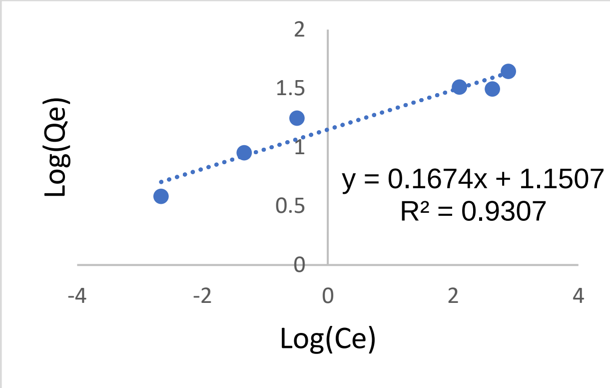

Figure 24: Freundlich isotherm for MCB

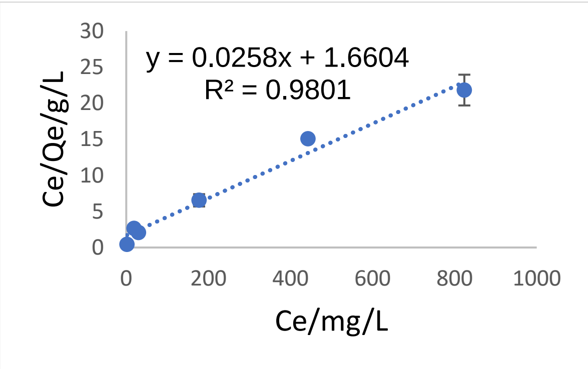

Figure 25: Langmuir isotherm for carbonised banana peel

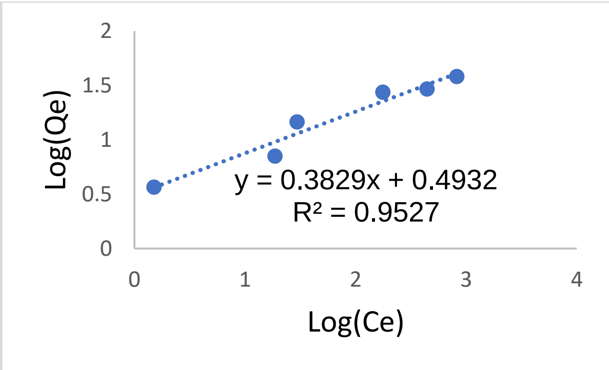

Figure 26: Freundlich isotherm for carbonised banana peel

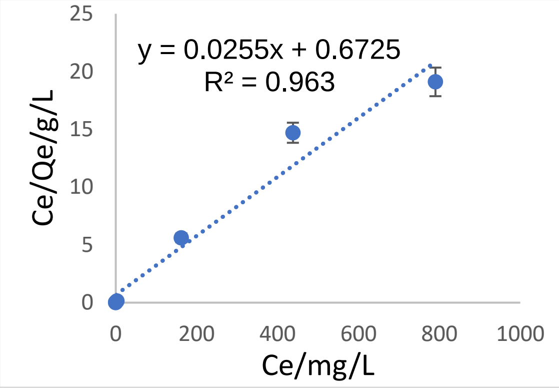

Figure 27: Langmuir isotherm for commercial AC

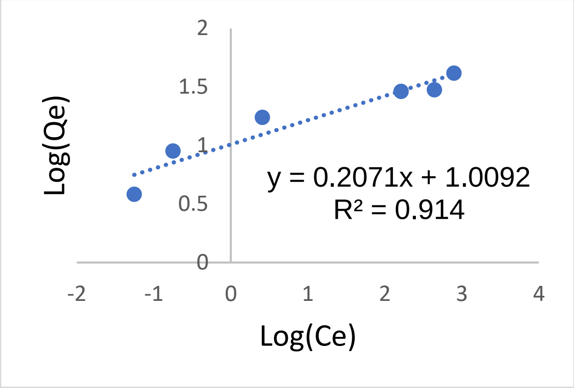

Figure 28: Freundlich isotherm for commercial AC

The isotherm parameters obtained are summarized in table 5.

Table 5: Isotherm parameters for different adsorbents on lead(II) ions

	Langmuir Isotherm Parameters		**Freundlich Isotherm Parameters**	
Adsorbent	q_m (mg/g)	R^2	n	R^2
MCB	41.3	0.961	5.97	0.931
Carbonised Banana Peel	38.8	0.980	2.61	0.953
AC	39.2	0.963	4.83	0.914

Comparison of the coefficient of determination (R^2) of the linearized forms of both isotherms suggests that the Langmuir model yields a better fit for the equilibrium adsorption data of lead(II) ions onto MCB, carbonised banana peel and AC. The maximum adsorption capacity, q_m, of MCB is the highest, followed by AC and carbonised banana peel.

Appendix B: Procedure for acid digestion of MCB

0.25g of the MCB sample was added to 10ml of 65% (w/w) nitric acid and stirred until no more brown and pungent nitrogen dioxide gas could be observed from the reaction. The mixture was then filtered into a 100ml volumetric flask and the volume made up to 100ml using deionised water. Three replicates were conducted for each MCB and a colorimeter was used to determine the concentration of iron in the solution. The mass of magnetite coating per gram of MCB was then calculated. The chemical equations for the reactions between magnetite (mixture of FeO and Fe_2O_3) and nitric acid are shown below:

$$FeO + 2\,HNO_3 \rightarrow Fe(NO_3)_2 + H_2O$$

$$Fe_2O_3 + 6\,HNO_3 \rightarrow 2\,Fe(NO_3)_3 + 3\,H_2O$$