Development of Nature-inspired Super-repellent Coating and Its Applications

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Abstract

Water pollution by industrial wastewater discharge has detrimental effects on the environment. In recent years, polydopamine (PDA) has emerged as a versatile coating material that enhances the adsorption capabilities and superwetting properties of a substrate, enabling it to remove a wide range of pollutants from wastewater including oil, dyes, and heavy metal ions either by filtration or adsorption. In this study, the effectiveness of PDA-coated as compared to unmodified filter paper and cotton wool in filtering water from diesel, as well as adsorbing dyes and heavy metal ions, were respectively investigated. A PDA coating on filter paper and cotton wool was first fabricated using a rapid one-step modification process involving the oxidation polymerisation of dopamine. While PDA-coated filter paper was used to filter an oil-water mixture, adsorption studies were conducted on PDA-coated cotton wool at varying concentrations. Results show that the percentage of pollutants adsorbed by PDA-coated cotton wool was generally higher than unmodified cotton wool, which can be attributed to the abundance of binding sites on polydopamine. Moreover, when PDA-coated filter paper was pre-wetted in diesel, it displayed underoil hydrophobicity and successfully separated diesel from water. Therefore, polydopamine has shown great potential to be a versatile coating material in the field of water purification.

1. Introduction

1.1. Literature Review

Only 0.007% of Earth's water is safe for human consumption (National Geographic, 2017). Yet, water pollution mainly arising from industrial activities and human negligence have caused water quality around the planet to deteriorate.

Oil spills released from oil-refining industrial processes cause a considerable negative impact on vegetation, marine environment, and agriculture (Chang, Stone, Demes, & Piscitelli, 2014). In 2010, the Deepwater Horizon oil spill occurred in the United States, releasing 4 million barrels of oil into the Gulf of Mexico which has had detrimental long-term impacts to marine biodiversity (McClain, Nunnally, & Benfield, 2019).

Dyes and heavy metal ions, which are dumped into water bodies by errant factories, also pose a serious threat to the environment due to their adverse health effects on organisms (Abu-El-Halawa, Zabin, & Abu-Sittah, 2016; Malik, Bashir, Qureashi, & Pandith, 2019). The discharge of dyes into water is undesirable as many of the dyes and their breakdown products are toxic, carcinogenic, and/or mutagenic to life forms, including methylene blue, malachite green and methyl orange (Suteu et al., 2009; Badar, 2012). Similarly, Cu^{2+} heavy metal ions can induce many serious neurodegenerative diseases in humans such as Alzheimer's disease, are toxic to many organisms and can lead to bioaccumulation especially in marine environments (Li et al., 2014; Liu, Ai, & Lu, 2014).

In the field of water purification, other than photocatalytic degradation and chemical coagulation, adsorption and membrane filtration are being explored. Among these methods, adsorption has proved to be the most efficient and widely used strategy due to its easy operation and fewer toxic byproducts (Liu et al., 2014). With the increasing demands for multifunctional advanced materials with super-antiwetting properties, great attention has also triggered scientists and researchers to focus on special wetting surfaces for a large number of functional applications (Li, Huang, Chen, Chen, & Lai, 2017) such as oil/water separation due to their different wettability to water and oil, such as being superhydrophobic and superhydrophilic, as well as superoleophilic and superoleophobic (Li et al., 2017). Researchers are now drawing inspiration from the wetting behaviour of natural organisms (Xiao, Wen, & Jiang, 2016), which hold promise for practical usage as they are low cost, readily available, sustainable and environmentally friendly (Mai, Das, Zhou, Lim, & Duan, 2020).

An example of wettability in nature is the secretion of proteinaceous byssus threads by mussels, which aid them in adhering to various substrates. The byssal cohesive and adhesive interactions achieved is due to the presence of post-transnationally modified amino acid residues such as L-β-3,4-dihydroxyphenyl-α-alanine (DOPA) (Li, Xia, Chen, Gao, & Zhan, 2018; Nicklisch & Waite, 2012). Polydopamine, a polymer also known as PDA, was discovered to have a similar molecular structure with DOPA, igniting research interest on using PDA as a coating material to improve the characteristics of a surface (Liu et al., 2014).

The chemical structure of PDA incorporates many functional groups such as catechol, amine and imine, which can offer a large number of active sites for binding heavy metal ions and organic pollutants via electrostatic interactions, coordination or chelation, hydrogen bonding, or π-π stacking interactions. (Liu et al., 2014). Therefore, it is unsurprising that PDA has emerged as a useful, versatile coating material that displays excellent biocompatibility.

In this study, PDA was coated on cotton wool for the adsorption of dyes and heavy metal ions. Cotton wool consists of 88% to 96.5% of cellulose, which has many −OH functional groups (Das & Karon, n.d.). These numerous hydroxy groups available on the surface of cellulose enable the easy adsorption of dyes and heavy metal ions. However, for oil-water separation, PDA was coated on filter paper instead as a proof of concept by carrying out separation through filtration.

This study aims to fabricate a PDA coating that is simple to produce and versatile which combines its adsorption capabilities with its superwetting properties to remove a wide range of pollutants from water, including diesel, dyes and heavy metal ions.

1.2. Objectives

- To investigate the effectiveness of PDA-coated filter paper as compared to unmodified filter paper in separating oil from water
- To investigate the effectiveness of PDA-coated cotton wool as compared to unmodified cotton wool in adsorbing dyes and heavy metal ions in water

1.3. Hypotheses

- PDA-coated filter paper will be more effective in separating oil and water from an oil-water mixture than unmodified filter paper
- PDA-coated cotton wool will be more effective in adsorbing dyes than unmodified cotton wool regardless of concentration
- PDA-coated cotton wool will be more effective in adsorbing heavy metal ions than unmodified cotton wool regardless of concentration

2. Materials and Methods

2.1. Materials

Dopamine hydrochloride, sodium periodate and potassium bromide were purchased from Sigma Aldrich. Methyl orange, malachite green and copper(II) sulfate were sourced from GCE Laboratory Chemicals. Methylene blue was procured from Unichem. Commercially available diesel was sourced from a petrol station. 55 mm Cat No 1003 055 filter paper was sourced from Whatman, 90 mm Grade 302 Qualitative Filter was sourced from Johnson Test Papers and cotton wool was sourced from Demann.

2.2. Surface Modification of Filter Paper and Cotton Wool

For the surface modification of filter paper, one piece of filter paper was first immersed in 100 cm^3 of acetate buffer (pH = 5) containing 0.400 g of sodium periodate in a conical flask. 0.200 g of dopamine hydrochloride was then added and left to stir on the orbital shaker for 1 hour 30 minutes. A concentration of 2.00 mg/cm^3 for dopamine hydrochloride was selected as polymerisation is optimised, leading to the production of a high density of nanoparticles and nanoprotrusions of homogeneous distribution (Mai et al., 2020). Appendix A delves deeper into the mechanism behind the oxidative polymerisation of dopamine. After that, the filter paper was taken out and washed under a strong flow of water to remove unbound particles and until neutral pH. Subsequently, it was dried in an oven at 60 °C overnight before using.

For the surface modification of cotton wool, the above procedure was repeated with 4.000 g of cotton wool instead of one piece of filter paper.

2.3. Oil-water Separation

2.3.1. Contact Angle Measurement

PDA-coated and unmodified filter paper were soaked in diesel. 10 µL of water was dropped as a single droplet on both soaked and non-soaked filter paper. A Dino-Lite USB Digital Microscope was used to capture close-up images of each droplet, after which their respective contact angles were measured using the ImageJ application. Five replicates were performed for each type of filter paper.

2.3.2. Gravity Filtration

Fluted unmodified and PDA-coated filter paper were folded and soaked in 2 cm^3 of diesel before being placed into a filter funnel after all diesel on the surface has flowed off. 3 cm^3 of diesel was added to 3 cm^3 of water to form an oil-water mixture to be filtered. Simple gravity filtration was conducted with the prewetted filter paper filtering the oil-water mixture. The filtrate was collected in a measuring cylinder. After 45 minutes of filtration when liquids were no longer passing through the filter paper, the volume of water and diesel in the filtrate was measured directly using the measuring cylinder.

The filtration efficiency, E, was calculated using the following formula (Liao, Tian, & Wang, 2017), where concentration was calculated by volume:

$$E = \left(1 - \frac{concentration\ of\ water\ in\ filtrate}{initial\ concentration\ of\ water}\right) \times 100\ \%$$

2.4. Batch Adsorption Studies with Dyes and Heavy Metal Ions

0.250 g of PDA-coated cotton wool and unmodified cotton wool was added to 40 ml of methylene blue, malachite green and methyl orange at 5 ppm, 10 ppm and 20 ppm concentrations, as well as 40 ml of copper(II) ions at 5 ppm, 10 ppm, 20 ppm and 30 ppm concentrations. The methylene blue and malachite green mixtures were shaken on an orbital shaker at 150 rpm for 1 hour 15 minutes while the malachite green and heavy metal ion mixtures were shaken for 45 minutes. The initial and final concentrations of the methylene blue, malachite green and methyl orange were analysed using a UV-vis Spectrophotometer (Shimadzu UV 1800) at 664 nm, 617 nm and 464 nm respectively, while that of copper(II) ions were analysed using a colorimeter (HACH DR890). Five replicates were conducted for each type of adsorbent, pollutant and concentration.

The percentage of pollutants adsorbed was calculated using the following formula:

$$Percentage\ adsorbed = \frac{initial\ concentration - final\ concentration}{initial\ concentration} \times 100\ \%$$

3. Results and Discussion

3.1. Characterisation of PDA Particles and PDA-coated Cotton Wool

Fourier-transform infrared (FTIR) spectroscopy analysis of both uncoated PDA particles and PDA-coated cotton wool showed stretching vibrations of hydroxy groups, as seen from the strong and broad peak at 3447 cm^{-1} for PDA particles and at 3424 cm^{-1} for PDA-coated cotton wool in Figure 1. These hydroxy groups are able to interact with and adsorb dyes such as by forming hydrogen bonds and heavy metal ions by acting as ligands and forming dative bonds. The FTIR spectra in Figure 1 are similar to those studied by Mai et al. (2020), suggesting that PDA has been successfully synthesised.

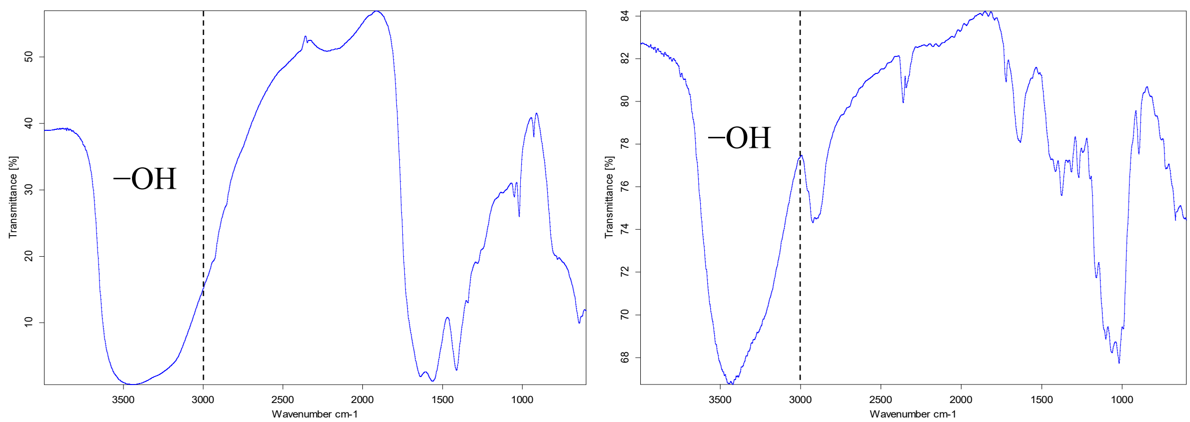

Figure 1: FTIR spectra of PDA particles (left) and PDA-coated cotton wool (right)

3.2. Oil-water Separation

3.2.1. Contact Angle Measurement

PDA-coated filter paper exhibited underoil hydrophobicity with a mean contact angle of 95.2 degrees (Figure 2, left). However, for unmodified filter paper, the water droplet was immediately absorbed into the filter paper upon contact before any photograph could be taken (Figure 2, right), which suggests a contact angle of 0 degrees and underoil superhydrophilicity.

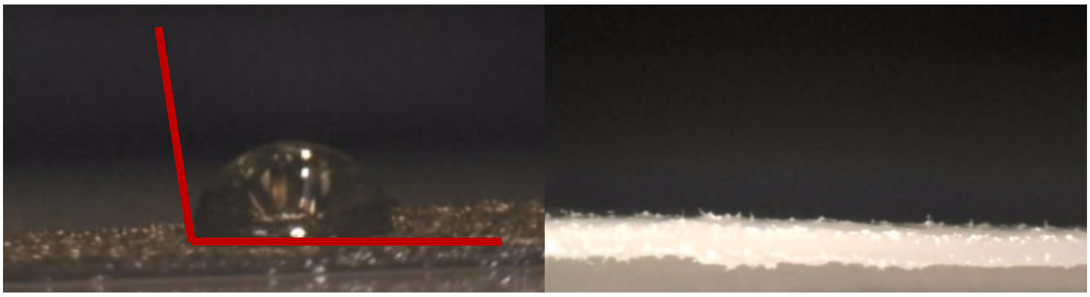

Figure 2: Underoil contact angle measurement of water on PDA-coated filter paper (left) and unmodified filter paper (right)

3.2.2. Gravity Filtration

PDA-coated filter paper demonstrated excellent separation capabilities of oil from water for a diesel-water mixture, while unmodified filter paper was largely unable to separate oil from water. Preliminary results in Figure 2 show that PDA-coated filter paper was able to remove 100 % of the water from the diesel-water mixture and the mean volume of diesel of collected as filtrate was 2.7 cm^3. This means that PDA-coated filter paper has a 100 % efficiency, as seen in Figure 3, possibly due to its low wettability to water when submerged in diesel. However, unmodified filter paper was not able to separate much water from the diesel-water mixture and only has a low efficiency of 8.8 % (Figure 3). The contact angle measurements once again support these results by showing that unmodified filter paper exhibits excellent wettability to water when submerged in diesel.

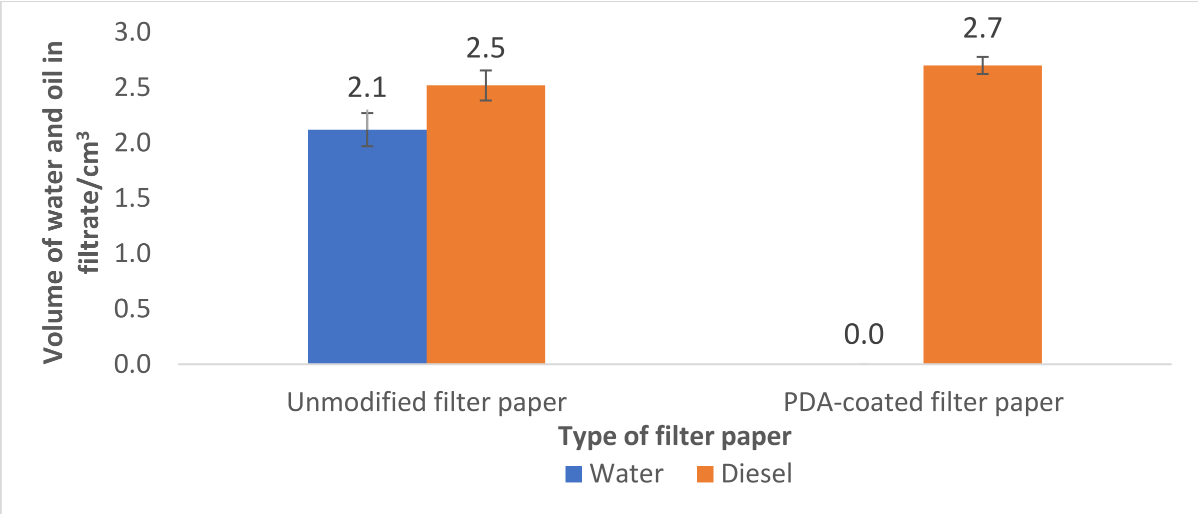

Figure 3: Volume of oil/water in filtrate after filtration by different types of filter paper

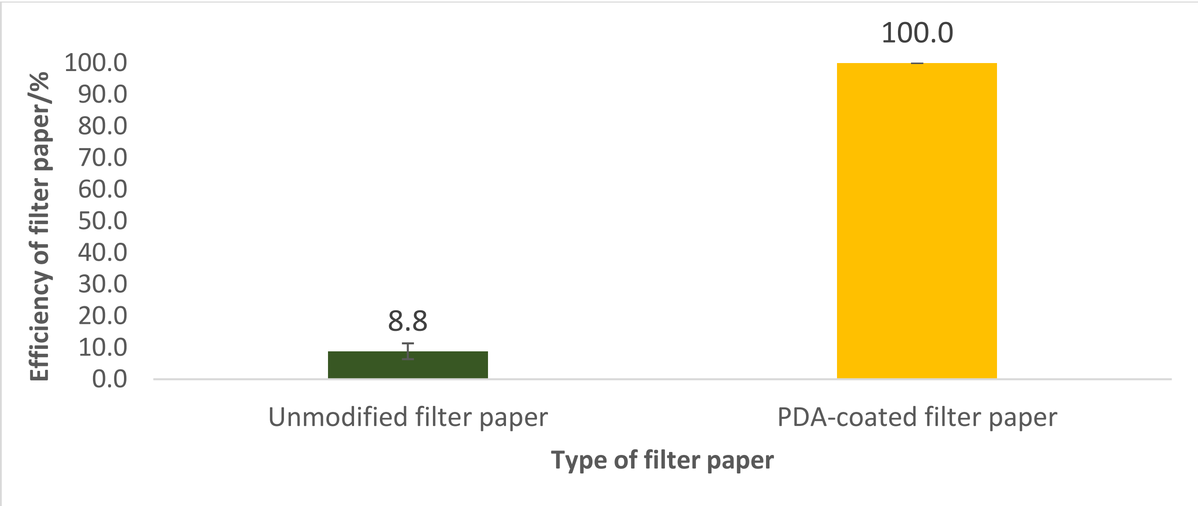

Figure 4: Efficiency of different types of filter paper for obtaining diesel as filtrate

3.3. Batch Adsorption Studies with Dyes and Heavy Metal Ions

3.3.1. Dyes

PDA-coated cotton wool adsorbed a higher percentage of dyes than unmodified cotton wool for all three dyes and at all concentrations included in this study (Figures 5-7). Mann-Whitney U-Tests were conducted between PDA-coated and unmodified cotton wool on the results for each dye at each concentration separately, which all gave p-values of below 0.05, indicating that there is a significant difference in the percentage of dye adsorbed, with the exception of methyl orange at 20 ppm where there is no significant difference (Table 1). This could be due to the saturation of methyl orange at higher concentrations as only 0.250 g of cotton wool was used as the adsorbent, which also accounts for the drops in percentage adsorbed as the concentration increases. Even though this is so, the results still suggest that unmodified cotton wool is completely ineffective in adsorbing methyl orange while PDA-coated cotton wool has some effect.

It is worth noting that although methyl orange is an anionic dye, which means that the positively charged hydroxy groups on cotton wool would not help in adsorption, the PDA-coated cotton wool was still able to adsorb a high percentage of the dye, which could be due to the presence of other functional groups such as amine and imine which are able to interact with the dye (Liu et al., 2014).

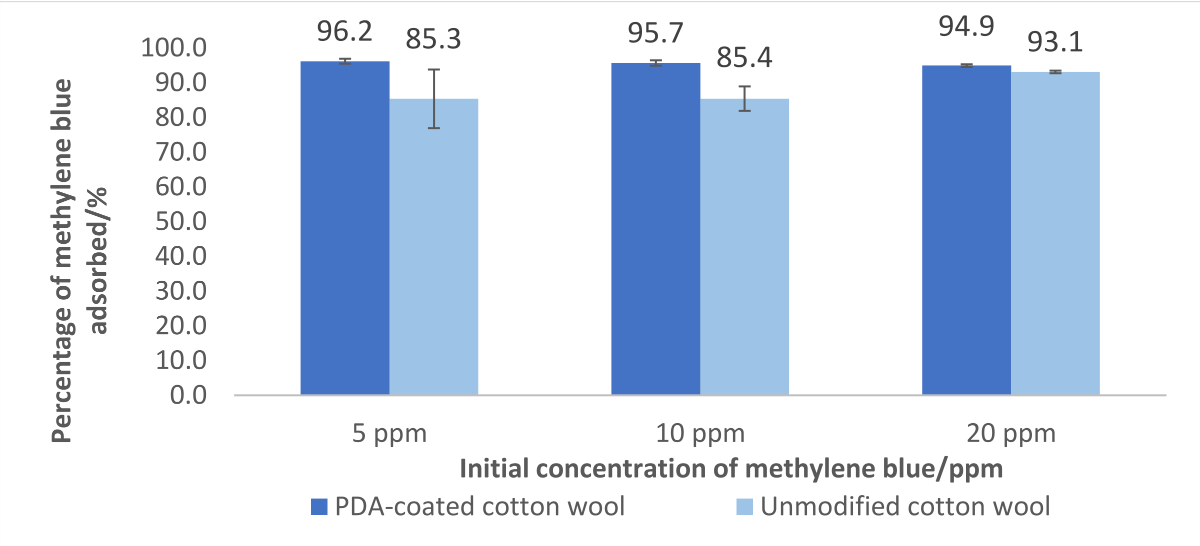

Figure 5: Adsorption of methylene blue by cotton wool at different concentrations

Figure 6: Adsorption of malachite green by cotton wool at different concentrations

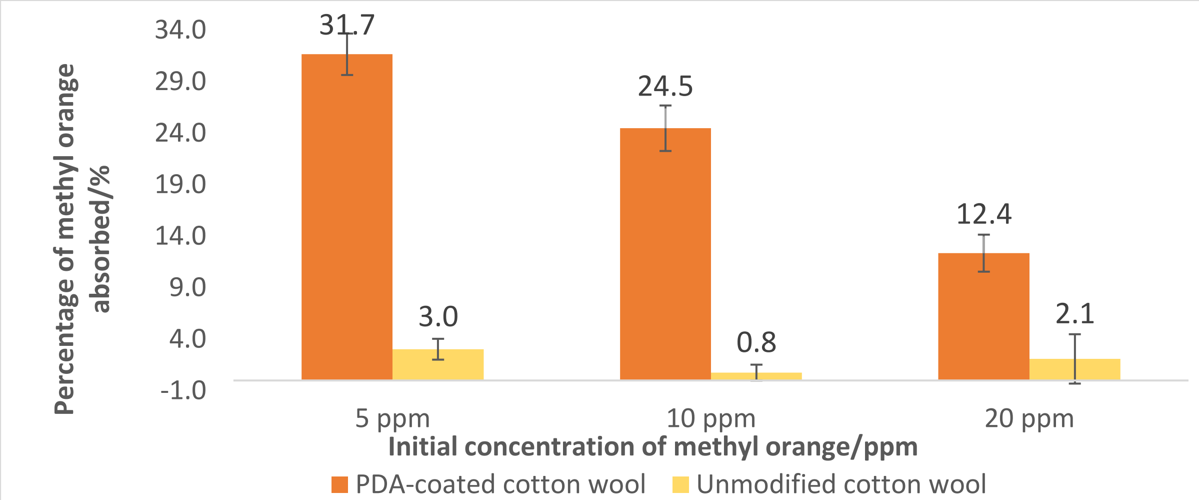

Figure 7: Adsorption of methyl orange by cotton wool at different concentrations

Comparison	Methylene blue		Malachite green		Methyl orange	
	P-value	Inference	P-value	Inference	P-value	Inference
PDA-coated cotton wool vs unmodified cotton wool	0.022	Significant	0.012	Significant	0.012	Significant
	0.012	Significant	0.012	Significant	0.012	Significant
	0.037	Significant	0.012	Significant	0.059	Insignificant

Table 1: Mann-Whitney U-Test of PDA-coated cotton wool against unmodified cotton wool

3.3.2. Copper(II) ions

PDA-coated cotton wool adsorbed a higher percentage of Cu^{2+} ions than unmodified cotton wool at 20 ppm and 30 ppm, but not for 5 ppm. Both had relatively similar adsorption capabilities at 10 ppm (Figure 8). Mann-Whitney U-Tests were conducted separately on the results for Cu^{2+} at 5 ppm, 10 ppm, 20 ppm and 30 ppm. The p-values of 5 ppm, 20 ppm and 30 ppm were 0.012 (<0.05), indicating that there is a significant difference in the results between the results for PDA-coated and unmodified cotton wool. For 10 ppm, the p-value was 1.000, indicating that the results were not statistically significant.

The decreasing percentage adsorbed by both PDA-coated and unmodified cotton wool as the concentrations increased could be attributed to the fact that only 0.250 g of cotton wool was used which caused a saturation of heavy metal ions. It is worth noting that PDA-coated cotton wool adsorbed a higher percentage of Cu^{2+} ions at higher concentrations (20 ppm and 30 ppm) as compared to unmodified cotton wool. This could be due to how PDA-coated cotton wool's adsorption ability of Cu^{2+} ions is highly dependent on solution pH (Liu et al., 2014).

The optimum pH where adsorption of Cu^{2+} ions is maximised is pH 5 (Farnad, Farhadi, & Voelcker, 2012) but in this study, the adsorption of Cu^{2+} ions was conducted under neutral pH conditions. This could have impacted the PDA-coated cotton wool's adsorption capabilities due to the formation of copper(II) hydroxide (Farnad et al., 2012). Therefore, at lower concentrations, PDA-coated cotton wool was at a disadvantage; at higher concentrations, this disadvantage diminishes, again due to a saturation of heavy metal ions.

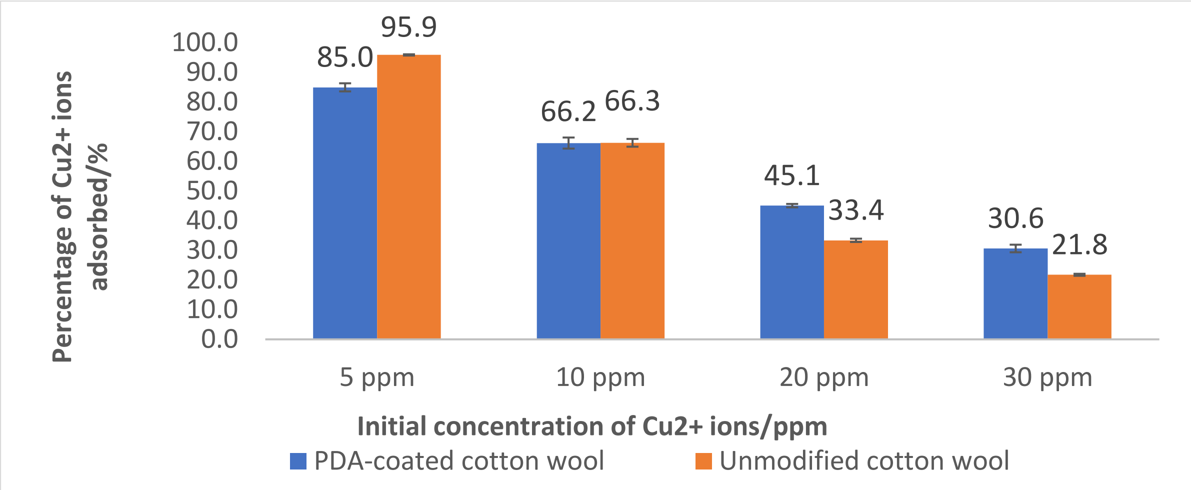

Figure 8: Adsorption of Cu^{2+} ions by cotton wool at different concentrations

4. Conclusions and Future Work

A polydopamine coating was successfully fabricated on the surfaces of cotton wool and filter paper using a rapid one-step modification process. For oil-water separation, PDA-coated filter paper was more effective in separating oil from an oil-water mixture than unmodified filter paper. For dye adsorption, PDA-coated cotton wool was more effective in adsorbing methylene blue, malachite green and methyl orange at all concentrations. For adsorption of Cu^{2+} ions, which has been chosen as a representative of heavy metal ions, PDA-coated cotton wool was more effective in adsorbing Cu^{2+} than unmodified cotton wool at 20 ppm and 30 ppm. Therefore, polydopamine exhibits interesting properties and has the potential to be a versatile material with wide-ranging applications in the field of water purification.

In the future, a greater variety of pollutants can be investigated to further explore polydopamine's capabilities. The experiment can be repeated with varying masses of adsorbent, adsorption time, pollutant concentrations and pH of mixtures. The polydopamine coating can also be further characterised such as by using a scanning electron microscope to examine its morphology. The reusability of a PDA-coated substrate can be studied. Finally, to further enhance hydrophobicity, the PDA backbone can be further modified through grafting.

References

Abu-El-Halawa, R., Zabin, S. A., & Abu-Sittah, H. H. (2016). Investigation of Methylene Blue Dye Adsorption from Polluted Water Using *Oleander* Plant (*Al Defla*) Tissues as Sorbent. *American Journal of Environmental Sciences, 12*(3), 213-224. doi:10.3844/ajessp.2016.213.224

Badar, H. (2012). Biosorptive Removal of Malachite Green, Methylene Blue and Methyl Orange Dyes from Aqueous Solutions by Ficus bengalensis (Banyan) Tree Leaves. *Asian Journal of Chemistry, 24*(7), 3070-3074. Retrieved from http://www.asianjournalofchemistry.co.in/User/ViewFreeArticle.aspx?ArticleID=24_7_54

Ball, V. (2018). Polydopamine films and particles with catalytic activity. *Catalysis Today, 301*, 196-203. doi:10.1016/j.cattod.2017.01.031

Chang, S. E., Stone, J., Demes, K., & Piscitelli, M. (2014). Consequences of oil spills: a review and framework for informing planning. *Ecology and Society, 19*(2). doi: 10.5751/es-06406-190226

Competing for Clean Water Has Led to a Crisis. (2020, April 6). Retrieved from https://www.nationalgeographic.com/environment/freshwater/freshwater-crisis

Das, A., & Kiron, M. I. (n.d.). Structure of Cotton Fiber. Retrieved from https://textilelearner.blogspot.com/2013/04/structure-of-cotton-fiber.html

Farnad, N., Farhadi, K., & Voelcker, N. H. (2012). Polydopamine Nanoparticles as a New and Highly Selective Biosorbent for the Removal of Copper (II) Ions from Aqueous Solutions. *Water, Air, & Soil Pollution, 223*(6), 3535-3544. doi:10.1007/s11270-012-1131-7

Lakshminarayanan, R., Madhavi, S., & Sim, C. P. (2018). Oxidative Polymerization of Dopamine: A High-Definition Multifunctional Coatings for Electrospun Nanofibers - An Overview. *Dopamine - Health and Disease*. doi:10.5772/intechopen.81036

Liao, Y., Tian, M., & Wang, R. (2017). A high-performance and robust membrane with switchable super-wettability for oil/water separation under ultralow pressure. *Journal of Membrane Science*, *543*, 123-132. doi:10.1016/j.memsci.2017.08.056

Li, J., Wang, W., Zhang, S., Wang, H., Xie, H., Shen, S., . . . Wang, B. (2014). Effects of chronic exposure to Cu2+ and Zn2+ on growth and survival of juvenile Apostichopus japonicus. *Chemical Speciation & Bioavailability, 26*(2), 106-110. doi:10.3184/095422914x13953450663379

Li, S., Huang, J., Chen, Z., Chen, G., & Lai, Y. (2017). A review on special wettability textiles: theoretical models, fabrication technologies and multifunctional applications. *Journal of Materials Chemistry A, 5*(1), 31–55. doi: 10.1039/c6ta07984a

Li, S., Xia, Z., Chen, Y., Gao, Y., & Zhan, A. (2018). Byssus Structure and Protein Composition in the Highly Invasive Fouling Mussel Limnoperna fortunei. *Frontiers in Physiology, 9*. doi: 10.3389/fphys.2018.00418

Liu, Y., Ai, K., & Lu, L. (2014). Polydopamine and Its Derivative Materials: Synthesis and Promising Applications in Energy, Environmental, and Biomedical Fields. *Chemical Reviews*, *114*(9), 5057–5115. doi: 10.1021/cr400407a

Mai, V. C., Das, P., Zhou, J., Lim, T. T., & Duan, H. (2020). Mussel-Inspired Dual-Superlyophobic Biomass Membranes for Selective Oil/Water Separation. *Advanced Materials Interfaces*, *7*(6), 1901756. doi: 10.1002/admi.201901756

Malik, L. A., Bashir, A., Qureashi, A., & Pandith, A. H. (2019). Detection and removal of heavy metal ions: A review. *Environmental Chemistry Letters, 17*(4), 1495-1521. doi:10.1007/s10311-019-00891-z

Mattson, J.S. & Mark, H.B. (1971). Activated Carbon: Surface Chemistry and Adsorption from Solution, New York: Marcel Dekker

McClain, C. R., Nunnally, C., & Benfield, M. C. (2019). Persistent and substantial impacts of the Deepwater Horizon oil spill on deep-sea megafauna. *Royal Society Open Science, 6*(8), 191164. doi:10.1098/rsos.191164

Nicklisch, S. C., & Waite, J. H. (2012). Mini-review: The role of redox in Dopa-mediated marine adhesion. *Biofouling, 28*(8), 865–877. doi: 10.1080/08927014.2012.719023

Suteu, D., Zaharia, C., Bilba, D., Muresan, R., Popescu, A., & Muresan, A. (2009). Decolorization wastewaters from the textile industry – physical methods, chemical methods [Abstract]. *Industria Textilă, 60*(5), 254-263. Retrieved from https://www.researchgate.net/publication/267394522_Decolorization_wastewaters_from_the_textile_industry_-_physical_methods_chemical_methods

Xiao, K., Wen, L., & Jiang, L. (2016). Bioinspired Superwettability Materials. *Kirk-Othmer Encyclopedia of Chemical Technology*, 1–34. doi: 10.1002/0471238961.koe00013

Appendix A: Oxidative Polymerisation of Dopamine

The mechanism for the oxidative polymerisation of dopamine is summarised in Figure 9. According to Ball (2018), dopamine (DA) first undergoes slow oxidation to form dopamine quinone (DQ) via dopamine semiquinone (DSQ). DSQ then goes through a Michael-type intramolecular cycloaddition reaction, resulting in the formation of leucodopaminechrome (DAL). Subsequently, DAL is oxidised and rearranged. Heteroaromatic 5,6-dihydroxyindole (DHI), as well as its oxidised product 5,6-indolequinone, are formed, which undergo branching reactions at positions 2, 3, 4 and 7. This causes the formation of an array of isometric dimers or higher-order oligomers which self-assemble to form a thin film coating of substrates.

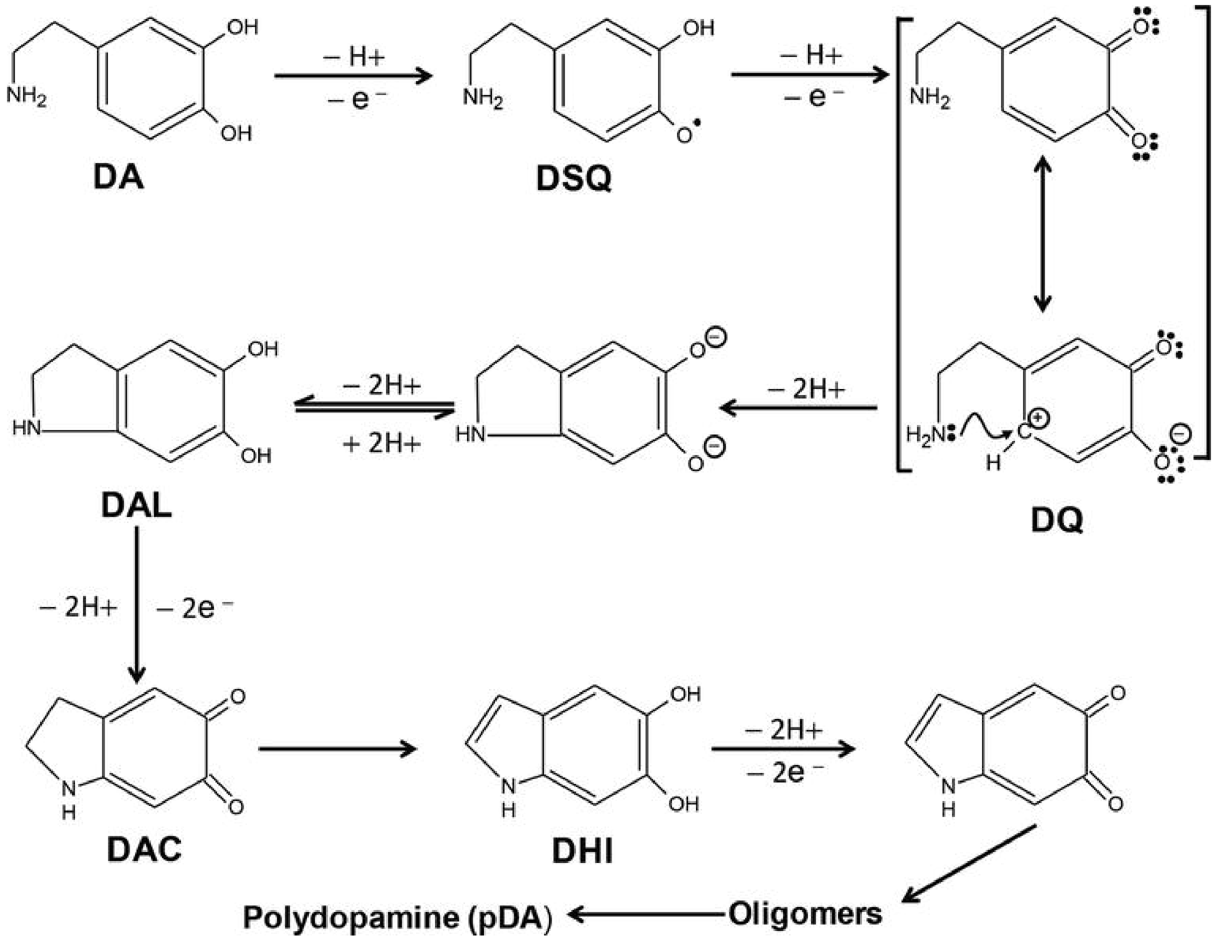

Figure 9: Mechanism for oxidative polymerisation of dopamine (Lakshminarayanan, Madhavi & Sim, 2018)