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Removal of waste dyes from water by organic wastes

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ABSTRACT

Dyes are coloured compounds that are used in cosmetics, clothing, plastics, textile, and many more industries. Dyes attach themselves to the surfaces to give them colour. Dyes are soluble in water and also make the water acidic. Organics dyes are toxic in nature and are one of the major contributing factors to water pollution because waste dyes are released into water bodies causing adverse effects on the aquatic environment. The dyes contain metal ions and other coloured compounds. Since dyes are organic compounds they are aromatic rings and hence also have nitro, sulfo, chloro, and amidocyanogen chains which can be hazardous. Releasing organic dyes can also cause inhibit aquatic plant growth, it can also be consumed by a human and cause diarrhea and it can also make the water carcinogenic. 'One way to remove waste dyes from water is adsorption. Adsorption is when molecules of a liquid, gas, or solution stick together to the surface of a solid, coating the solid (adhesion). The solid surfaces that they stick to are called sorbents. Sorbents are insoluble materials that are used to collect liquids by either absorption or adsorption. The three types of sorbents are Natural organic sorbents, Natural inorganic sorbents, and Synthetic sorbents (man-made materials).'[5] In some places, dyes are removed from water using activated carbon but it is expensive and preparing it with the optimum conditions consumes a lot of energy, which prevents it from being used on a larger scale. The goal of this research is to show that Natural organic sorbents can be used to remove dyes from water as this is a more efficient, cheap, and most importantly environment-friendly method by measuring the turbidity of a solution.

Keywords: *Dyes, Organic Solvents, Water Pollution, Adsorption*

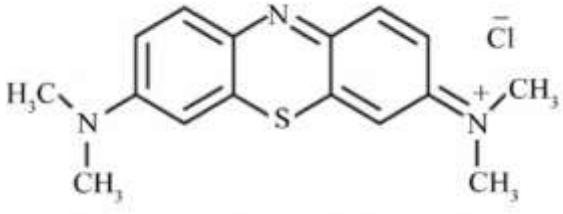
1. RESEARCH QUESTION

What is the effect of different types of organic sorbents (Mango peel, Apple peel, Banana peel, Vegetable peel, Dry Grass powder, and Dry leaves powder) on the rate of adsorption of methylene blue dye of different concentrations (0.15M, 0.25M, 0.35M, 0.45M,0.55M).

2. INTRODUCTION

I visited my dad's factory when I was younger and he took me to his friend's clothing factory where he showed us around. My dad and his friend started talking about the dyeing process and how they had to treat the waste dye before throwing it out into water bodies because the rules had become severe.

The owner also mentioned how there were a lot of companies who were still throwing out the dye without treating it. '*Methylene blue is one such dye, it is soluble in water and it has antioxidant, antimalarial, antidepressant, and cardioprotective properties.'*[10]



"Figure 1-Chemical Structure of Methylene Blue dye (MB)"[7]

It is used in industries where dying is needed and it is also used as a medicine in the form of an injection to treat methemoglobinemia. Methemoglobinemia occurs when the blood cannot deliver oxygen to the body parts that need it.

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Using fruit peels for removing dyes from water is cheaper, efficient, and more environmentally friendly than using activated carbon, coagulation, Ozonation, Electrochemical process, etc.

"The Beer-Lambert law states that the absorptive capacity of a substance is proportional to the concentration of the substance in the solution. This can be expressed as A = εlc, where A is absorbance, ε is the molar extinction coefficient (which depends on the nature of the chemical and the wavelength of the light used), l is the length of the path light must travel in the solution in centimetres, and c is the concentration of a given solution"[2]

Sorbents

"Sorbents are insoluble materials or mixtures of materials used to recover liquids through the mechanism of absorption, or adsorption, or both. Absorbents are materials that pick up and retain liquid distributed throughout its molecular structure causing the solid to swell (50 percent or more). The absorbent must be at least 70 percent insoluble in excess fluid. Adsorbents are insoluble materials that are coated by a liquid on their surface, including pores and capillaries, without the solid swelling more than 50 percent in excess liquid. To be useful in combating oil spills, sorbents need to be both oleophilic (oil-attracting) and hydrophobic (water-repellent). Although they may be used as the sole cleanup method in small spills, sorbents are most often used to remove final traces of oil, or in areas that cannot be reached by skimmers. Sorbent materials used to recover oil must be disposed of in accordance with approved local, state, and federal regulations. Any oil that is removed from sorbent materials must also be properly disposed of or recycled." [5]

'There are three types of sorbents:

- *Natural organic sorbents, eg-straw, hay, sawdust, ground corncobs, feathers, and other readily available carbon-based products.*
- *Natural inorganic sorbents, eg- clay, perlite, vermiculite, glass wool, sand, or volcanic ash.*
- *Synthetic sorbent (man-made materials), eg- plastics, such as polyurethane, polyethylene, and polypropylene'*[5]

Turbidity

"Turbidity is the measure of relative clarity of a liquid. It is an optical characteristic of water and is a measurement of the amount of light that is scattered by material in the water when a light is shined through the water sample. The higher the intensity of scattered light, the higher the turbidity."

"High concentrations of particulate matter affect light penetration and ecological productivity, recreational values, and habitat quality, and cause lakes to fill in faster. In streams, increased sedimentation and siltation can occur, which can result in harm to habitat areas for fish and other aquatic life. Particles also provide attachment places for other pollutants, notably metals and bacteria. For this reason, turbidity readings can be used as an indicator of potential pollution in a water body"

"Excessive turbidity, or cloudiness, in drinking water is aesthetically unappealing, and may also represent a health concern. Turbidity can provide food and shelter for pathogens. If not removed, the causes of high turbidity can promote regrowth of pathogens in the water, leading to waterborne disease outbreaks, which have caused significant cases of intestinal sickness throughout the United States and the world."[11]

'Turbidity is measured with a meter called turbidity meter and it is measured in Nephelometric Turbidity Units (NTU) which basically is the comparison of the amount of light scatter in a water sample and the standard reference solution'[1]

Different types of dyes

"Dyes are colored compounds which are widely used in textiles, printing, rubber, cosmetics, plastics, leather industries to color their products results in generating a large amount of colored wastewater. Mainly dyes are classified into anionic, cationic, and non-ionic dyes. Among all the dyes using in industries, textile industries placed in the first position in using of dyes for coloration of fiber . Dyes are chemical compounds which attach themselves to fabrics or surface shells to impart color. Depolarization of waste water from textile and manufacturing industries is a major challenge for environmental managers as dyes are water soluble and produce very bright colors in water with acidic properties. It has been projected that textile and manufacturing industries are using more than 10,000 commercially available (worldwide) dyes and the consumption of dyes in textile industry is more than 1000 tones/year and about 10-15% of these dyes are discharged into waste streams as effluents during the dyeing processes."[9]

'Synthetic dyes have variety of structures and the types of dyes that are used often on an industrial scale are the azo, anthraquinone, sulfur, indigoid, triphenylmethyl (trityl), and phthalocyanine derivatives. But azo derivatives are undoubtedly the most frequently used'[6]

Use of different dyes

"Azo dyes are the most used dyes and account for more than 60 % of total dyes. Approximately 70 % of all the dyes used in industry are azo dyes. These compounds are characterized by the functional group (-N=N-) uniting two symmetrical and/or asymmetrical identical or non-azo alkyl or aryl radicals.

Azo dyes are the most important synthetic colorants which have been widely used in textile, printing, paper manufacturing, etc. The azo dyes are distributed according to the number of azo linkages which is in the same molecule of the dye such as monoazo, disazo,

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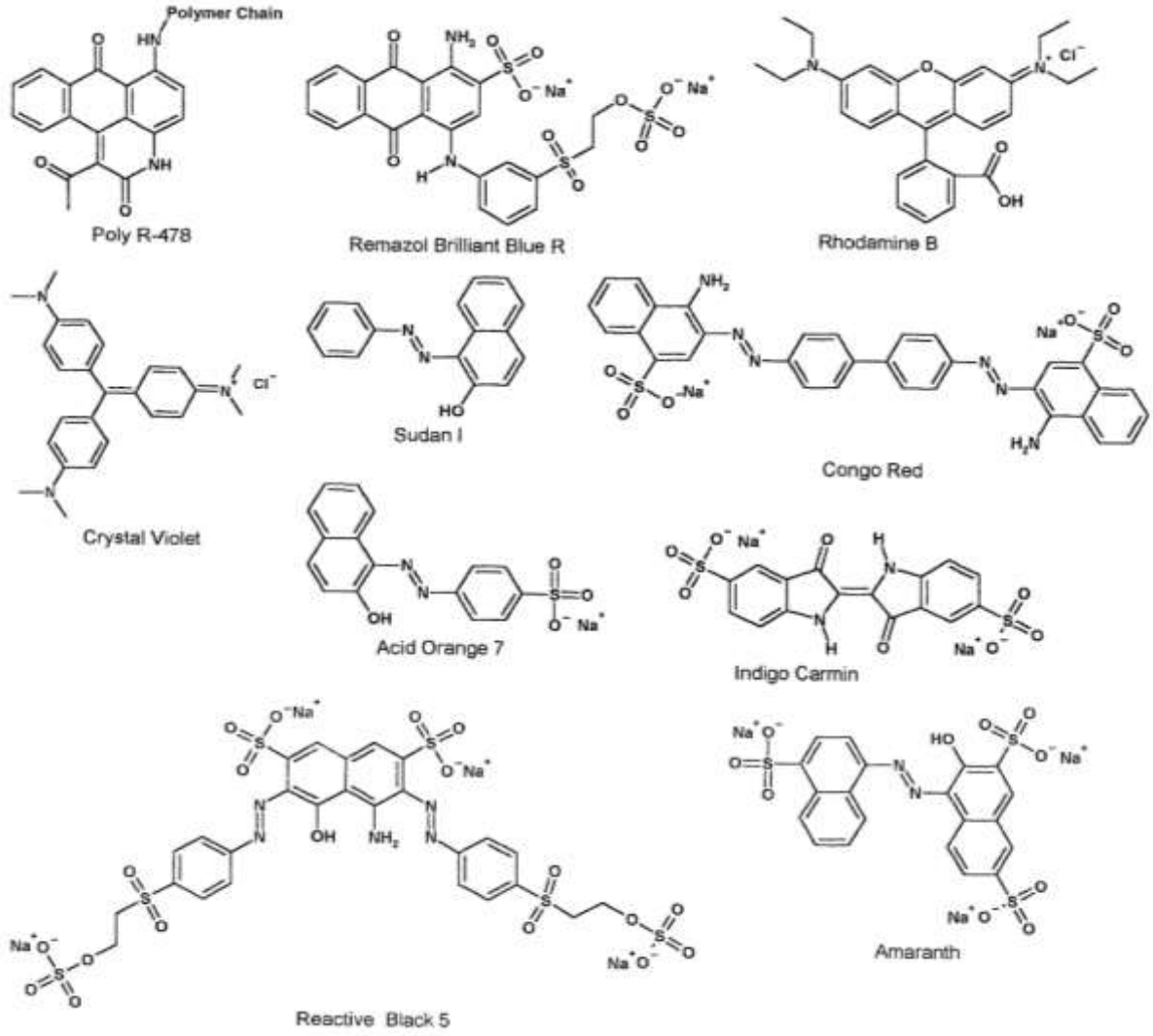
trisazo, polyazo and azoic."[6]

'Monoazo:chrysoidine(dyes cotton), Yellow basic dye(used for coloring cellulosic fibers), Orange IV, orange dye Diazo: Brown dye structure, blue direct dye, orange direct dye.

Polyazo: direct red dye (for dyeing leather, with dark shades: red, brown and dark black).'[3]



"Figure 2- chemical structure of some synthetic dyes"[6]

Seeding (alum)

"Crystal seeding is the process of adding homogeneous or heterogeneous crystals to a crystallising solution to nucleate and/or grow more crystals. Seeding has emerged as one of the most critical steps in optimising the crystallisation Process"[8]

The harmful effect of dye on the water table.

"The water in the rivers have the color of the dye the factories produce that day. The soil in which people grow their food becomes toxic, as they use the water for farming. The rivers are dead, as fish and plants can't survive the chemicals that the factories dump into the rivers."[4]

The harmful effect of heavy metals on human beings

"The formation of a carcinogenic amine from the dye Direct Blue 14 by human skin bacteria (Platzek et al., 1999) and the antifungal activity of 13 diazobenzene dyes have been established (Oros et al., 2001). As several thousand different synthetic dyes that are employed exhibit various biological activities, it is understandable that our knowledge concerning their behavior in the environment and health hazards involved in their use is still incomplete.
Different diseases caused by dye if it is intaken with drinking water"[9]

3. HYPOTHESIS

Methylene blue is an oxidation-reduction agent and it is formed when a compound consisting of dark green crystals or crystalline powder is dissolved in water or alcohol giving a dark blue solution. Fruit peel is a natural organic sorbent, it is very good and effective. So according to the Beer-Lambert law, I predict that as the concentration of methylene blue in the solution increases, the

rate of adsorption by the dried natural sorbents will also increase. I also predict that the dried leaves and grass will be the most effective sorbents compared to the fruit and vegetable peel powder. Then I think that banana peel would be most effective followed by apple peel, mango peel, and vegetable peel.

4. LITERATURE REVIEW

The methodology that is being used here is turbidity and it basically measures how cloudy or unclear the water is by the amount of light that is scattered. So, the turbidity decreases with time as the sorbents adsorb the dye over time.

The strength of this research is that organic waste products are being used to remove waste dyes from water which is not only cost-effective but also environmentally friendly. The weakness of this research is that we weren't able to bring more sorbents into this research.

Further research that could be conducted related to this is to determine what amount of peel/dried sorbent is required to remove all of the dye in the water. An electron microscope can also be used to see the sorbents in detail and how they absorb the dye.

Another research can also be conducted to compare it to other ways of dye removal for example using graphene or by other processes such as coagulation or ozonation.

5. VARIABLES

Independent Variables	Concentration of methylene blue (0.15M, 0.25M, 0.35M, 0.45M, and 0.55M) The molecular formula of methylene blue is $C_{16}H_{18}ClN_3S$, so its Molecular weight is 319.5g. So, for 0.15M, 4.8g of methylene blue dye is added to $100cm^3$ of water. 0.25M, 8.0g of methylene blue dye is added in $100cm^3$. 0.35M, add 11.2g of methylene blue dye to $100cm^3$. 0.45M, add 14.4g of methylene blue to $100cm^3$. 0.55M, 17.6g of methylene blue to $100cm^3$.
Dependent Variables	The measurement of water clarity by the amount of light scattered (in Nephelometric Turbidity Units/NTU)

Controlled Variable	**Method of control**	**Possible effect on results**
sorbents source	All the grass, leaves, vegetables, and fruit peels used should be from the same region. The preparation for all the sorbents should be the same.	If the sorbents are prepared differently then it could affect the rate of adsorption of the dyes.
Use of micropipette	To add an accurate amount of water to make different concentrations of methylene blue. Also, to maintain the volume of all the concentrations of methylene blue solutions.	If the volumes of the solutions are not the same then it will give inaccurate results.
The concentration of methylene blue solution	Only using distilled water to make the differently concentrated solutions of methylene blue	If normal water is used, some impurities could be present in the solutions.
The time for which the sorbents are dried for	Drying the grass, leaves, vegetables, and fruit peels for 30 minutes to an hour in the microwave oven.	If the grass, leaves, vegetables, and fruit peels are dried for too long, they will burn and turn black.
Using a digital balance	This will allow adding the methylene blue dye to the solution more accurately	If the mass of methylene blue dye is not accurate, it will give an inaccurate concentration and affect the results.

Uncontrolled	**A possible method of control**	**Possible effect on results**
Size of the fruit and vegetable peel	As the dried fruit and vegetable peels	The size of particles affects the rate of

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	are going to be ground with the same blender, it is assumed that the peels are the same size.	adsorption of methylene blue.

6. APPARATUS

- 5 grams of 10 fruit peels
- 1 Turbidity meter
- Dropper
- Electronic weighing balance
- 5 concentrations of methylene blue solution each being 5 cm^3(0.15M, 0.25M, 0.35M, 0.45M, and 0.55M) $C_{16}H_{18}N_3SCl$

7. HAZARDS

Hazard	Control measure
Safety: Methylene blue solution will stain your skin	Wearing gloves while measuring its volume and transferring it.
Environmental: Disposal of leaves, grass, vegetable and fruit peel and solution containing methylene blue dye.	The methylene blue solution should be diluted to less than 1M concentration and then it can be poured down the drain.

8. PROCEDURE

1. The fruit peels (mango peel, apple peel, banana peel, vegetable peel, grass, and leaves) have to be washed with tap water and then with distilled water.
2. Keep the fruit peel in an oven for 30 minutes to almost an hour at 60℃.
3. After drying the sorbent (mango peel, apple peel, banana peel, vegetable peel, grass, and leaves), grind it in a blender so it forms a powder, and then sift that powder through a sieve of 1mm.
4. Take a 250 cm^3 flask or beaker and add 4.8g of methylene blue in 100cm^3 of distilled water to make a 0.15M methylene blue solution. Then keep it in a dark place. Repeat this for other concentrations:0.25M(8.0g of methylene blue dye is added in 100cm^3), 0.35M (add 11.2g of methylene blue dye to 100cm^3), 0.45M (add 14.4g of methylene blue to 100cm^3), 0.55M (17.6g of methylene blue to 100cm^3). And keep them all in a dark place.
5. Using a dropper/micropipette take the methylene blue solution without dried sorbents in a cuvette and place it on a turbidity meter.
6. Record the NTU of methylene blue without the fruit peel in it.
7. Add 2 grams of the powdered sorbents (apple peel, banana peel, orange peel, sugarcane straws, rice husk, mango peel, coconut husk/coir, lemon peel, pomegranate peel, pomelo peel) to 10cm^3 of the methylene blue solutions of different concentrations and keep it in for one hour.
8. Using a dropper/micropipette take the solution without fruit peel in a cuvette and place it on a colorimeter.
9. Record the NTU with all five fruits peeled.

9. RESULTS

Sr. No	Time Taken Minutes	Dry Grass Powder	Dry Leaves Powder	Dry Mango Peel Powder	Dry Apple Peel Powder	Dry Banana Peel Powder	Dry Vegetable Peel Powder
1	0	652	652	652	652	652	652
2	5	433	411	524	583	615	627
3	10	291	283	332	482	567	592
4	15	264	259	311	423	512	543
5	20	222	219	287	390	487	511
6	25	208	205	263	351	441	472
7	30	198	196	233	311	400	429
8	35	189	185	209	278	367	387
9	40	166	163	183	249	325	349
10	45	161	158	152	219	289	308
11	50	154	151	144	189	257	283
12	55	144	134	131	155	239	252
13	60	138	121	129	129	222	221
14	65	134	120	127	127	211	190
15	70	130	119	125	125	197	184
16	75	127	118	123	123	186	177
17	80	124	117	121	121	173	171
18	85	121	116	119	119	164	164
19	90	118	115	117	117	155	157
20	95	115	114	117	116	141	157
21	100	115	114	117	116	141	157

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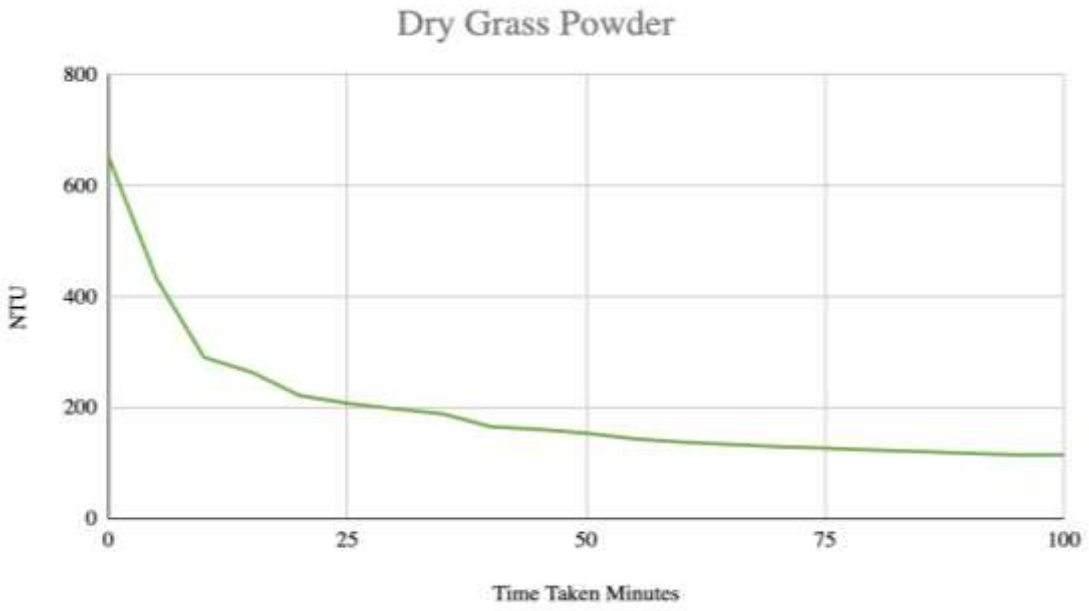

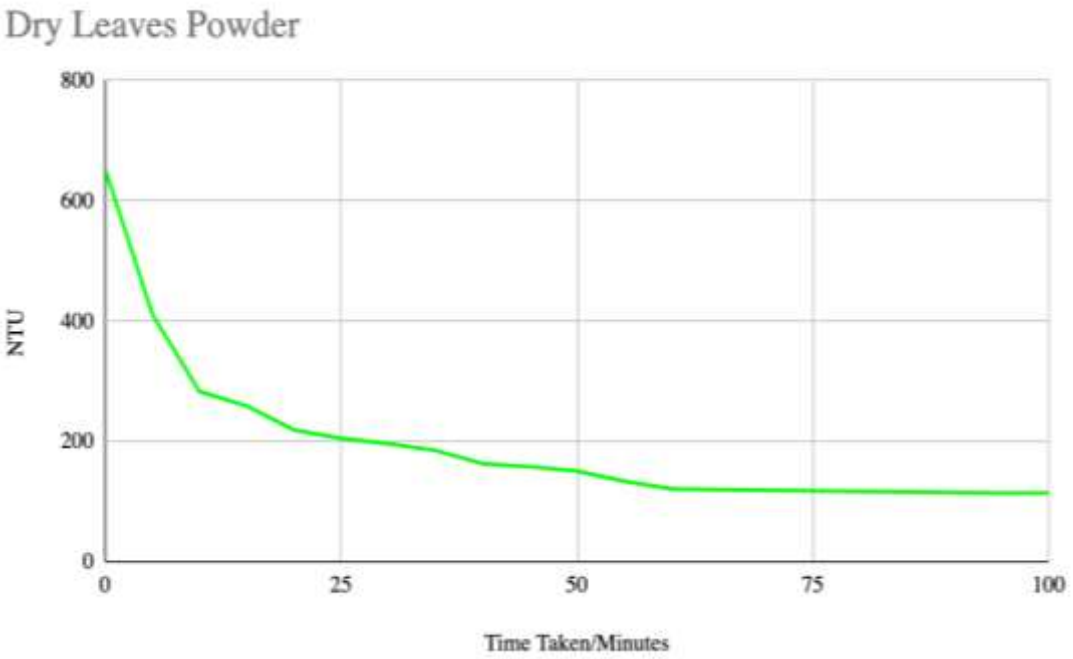

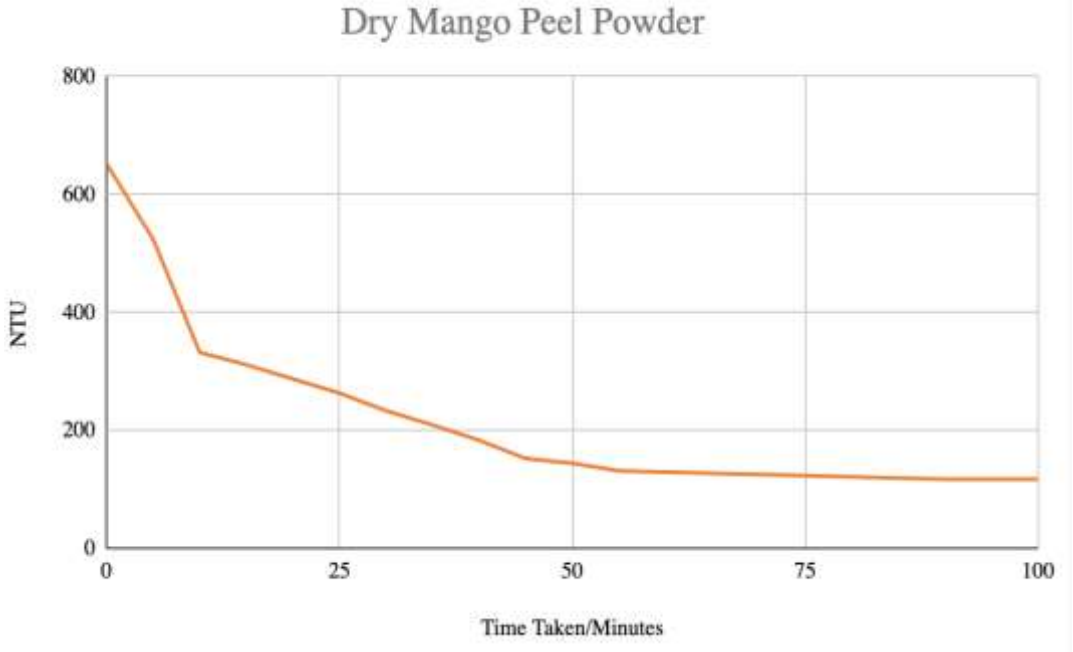

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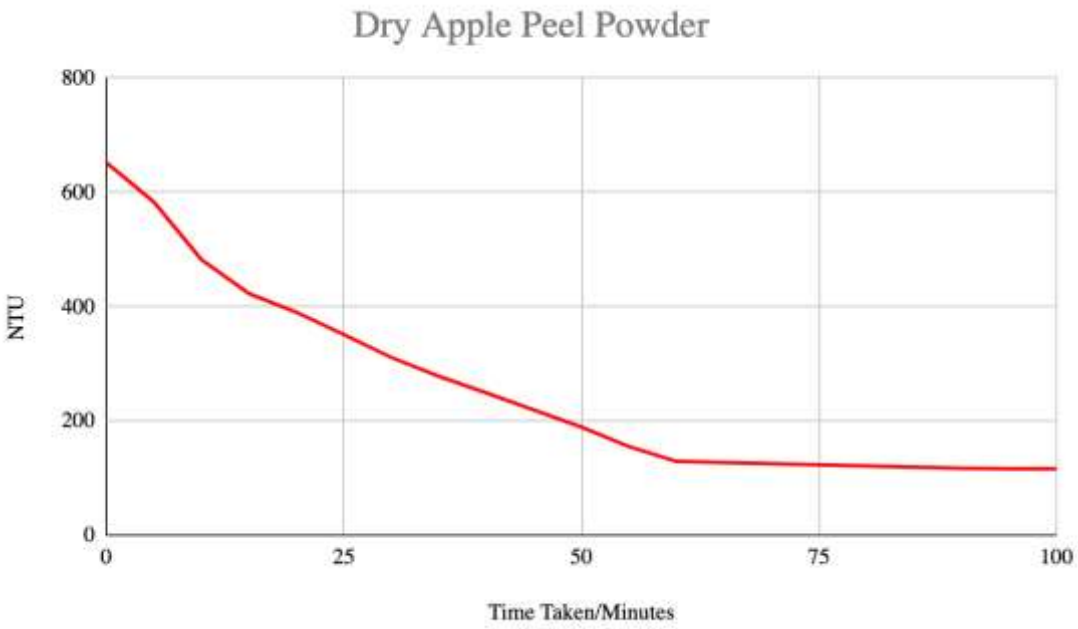

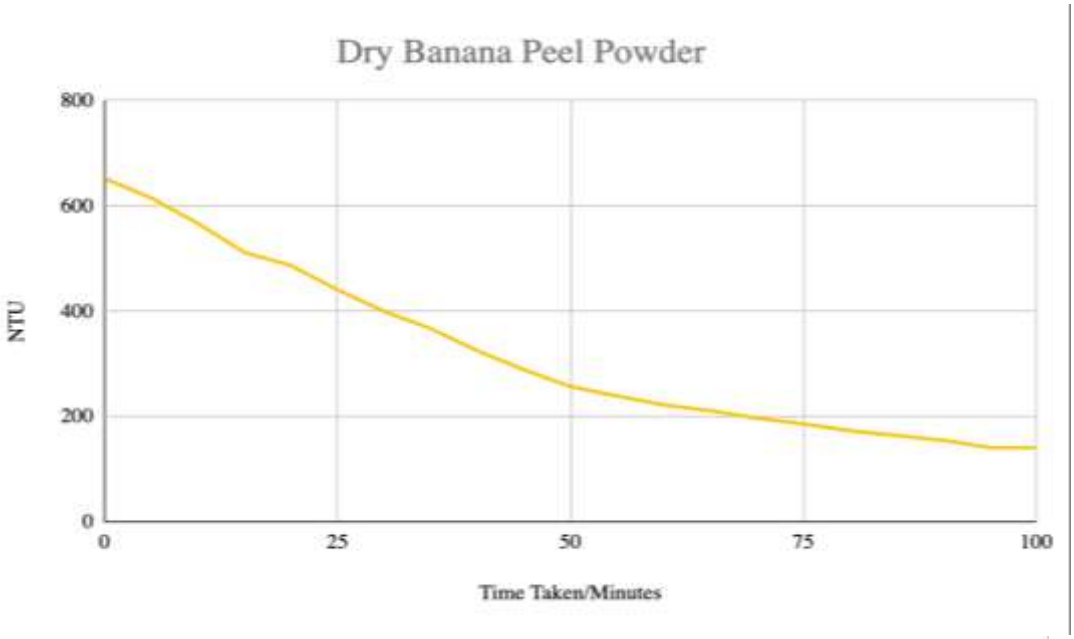

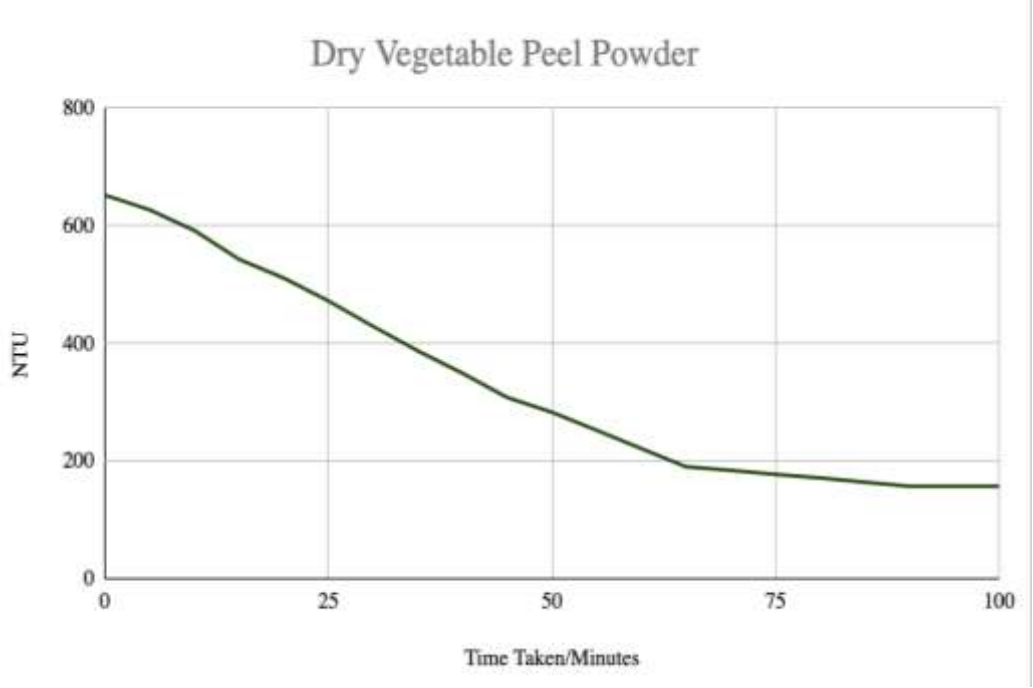

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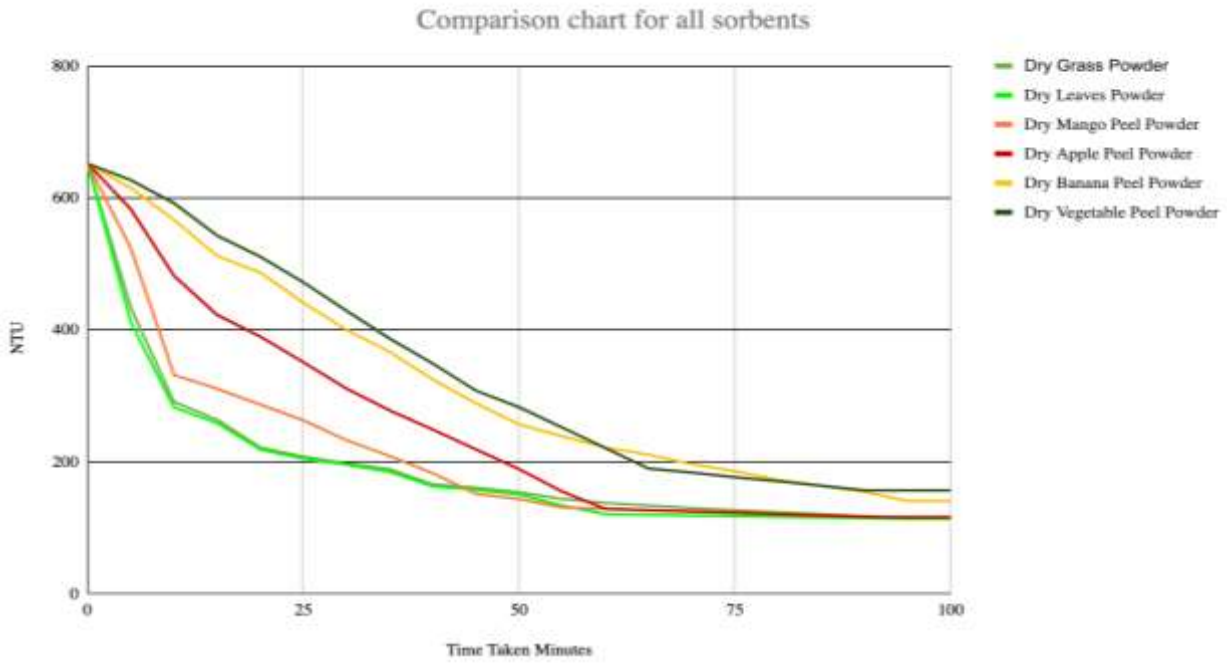

10. DISCUSSION

- In the graph for dry grass powder: the rate of decrease of tubidity in first 10 minutes (652-291 NTU-36.1 NTU/minute) the rate then gradually decreases as the steepness of the curve decreases and eventually levels off
- The overall shape of the graph for dry leaf powder is similar to the dry grass powder except it is only slightly steeper which showers that it has a higher rate in the first 10 minutes (36.9 NTU/minute) and is a more effective sorbent. This sorbent also decreased the tubidity of water the most.
- As the time increases the turbidity (in NTU) for all the 6 sorbents decreases as the intensity of the scattered light decreases as the sorbents are adsorbing the dye. So, all the sorbents are effective.
- Dry leaves powder has the highest overall rate which is 5.38 NTU per min, followed by (dry grass powder (5.37 NTU per min), apple peel powder (5.36 NTU per min), mango peel powder (5.35 NTU per min), dry banana peel powder (5.11 NTU per min) and dry vegetable peel powder (4.95 NTU per min)
- As seen in the graph and the table the turbidity of the solution keeps decreasing until it becomes constant and levels off.
- The turbidity of the solution with dry leaves powder at the end (100 minutes) is the least (114 NTU). So, the dry leaves are the most effective sorbent.
- In all the solutions the turbidity decreases rapidly at first and then the rate slows down and then becomes constant. As seen in the graph the steepest decrease in turbidity is shown by the dry leaves powder followed by dry grass powder, mango peel powder, apple peel powder, banana peel powder and then vegetable peel powder.

11. CONCLUSION

The experiments show that all the dried sorbents used (mango peel, apple peel, banana peel, vegetable peel, grass, and leaves) were effective. The dry leaves powder was the most effective sorbent. This shows that low-cost sorbents which are basically organic wastes can be used instead of expensive methods/sorbents to remove waste dyes from water. This experiment is beneficial for the environment as it shows that the waste from fruits can remove harmful and toxic substances from water. This will keep water bodies free from hazardous chemicals and is also a cheap and efficient way of doing so. More research can be done on this to find out cost-efficient and environmentally friendly ways to remove other industrial effluents from water.

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