

BIOSORPTION OF HEAVY METALS, DYES AND PHENOL USING PHOSPHORIC ACID MODIFIED RICE HUSK

G.Parthiban* and M.S.F.Rifna

Department of Chemistry, Faculty of Science, Eastern University Sri Lanka. Email: parthig24@yahoo.com*

ABSTRACT

The removal of contaminants from wastewater is still far away from a satisfactory solution. In fact, the selection of a particular wastewater treatment technology should not be based uniquely on its efficiency, but should rather integrate environmental and economical aspects. Within this framework, the main objective of this study is the removal of various contaminants in wastewater including heavy metals (Cadmium and Copper), dyes (Methyl Red and Methylene Blue) and Phenolic compounds via an environmental friendly green technology method. In this study, grounded rice husk was examined as sorbent material which was chemically modified with Phosphoric acid (1.0 M) and was found to be effective in removing the contaminants. Batch studies were performed on synthetic wastewater at room temperature to evaluate the effects of various parameters such as contact time, pH, initial concentration of the solution and adsorbent dose on removal efficiency of the pollutants. The experiment was also applied to treat two samples of industrial wastewater containing Cadmium and Carmoisine E122. The removal efficiency was found to be pH dependent. The removal efficiency was higher for Phenol and Methyl Red at low pH values and it was shown that the removal efficiency was higher for heavy metals and Methylene Blue at higher pH values. The equilibrium reached nearly in 2 hours for all the contaminants. Equilibrium sorption data were fitted into Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherms. Of the four adsorption isotherms, the R^2 value was higher for D-R isotherm for the adsorption of Cadmium (0.979), Freundlich isotherm for the adsorption of Copper (0.945), Freundlich isotherm for the adsorption of Methyl Red (0.994), Temkin isotherm for the adsorption of Methylene Blue (0.953) and Langmuir isotherm for the adsorption of Phenol (0.987). Adsorption data were well described and adsorption isotherm constants were determined from the respective adsorption isotherm equations. The present study analyzed the adsorption efficiency of rice husk and concluded that treated rice husk gave comparatively better adsorption efficiency. The treated rice husk can be implemented on large scale industrial applications after field studies.

Key words: Adsorption isotherm, Heavy metals, Phenol, Rice husk, Wastewater

1. INTRODUCTION

Water pollution raises a great concern nowadays since water constitutes a basic necessity in life and thus, is essential to all living things. The major hindrance is the simultaneous existence of different types of pollutants such as dyes, heavy metals, Phenols, pesticides and pharmaceuticals. Heavy metal ions are reported as priority pollutants due to their mobility in natural water ecosystems.¹ They have adverse impacts on human health such as allergies, hyper pigmentation, skin irritation, skin cancer, neurological effect, hypertension,

cardiovascular diseases and pulmonary diseases.² Copper, an element which has been used by man for years, can be regarded as a longstanding environmental contaminant. The World Health Organization (WHO) recommended that the maximum acceptable concentration of Cu (II) in drinking water is 1.5 mg/L.³ Cadmium is a very toxic element affecting the environment. Once absorbed, Cd is efficiently retained in the human body, in which it accumulates throughout life.⁴ Cd is primarily toxic to the kidney. Cd can also cause bone demineralization.⁴ Human beings have reported nausea and vomiting at levels of 15 mg/L Cadmium, with no adverse effect at 0.05 mg/L.⁵ Dyes and pigments are one of the problematic groups of pollutants. Of all available dyes, Methylene Blue (MB) is most commonly used in industries such as textiles and pharmaceuticals. Methylene Blue (MB) is a basic aniline dye with the molecular formula $C_{16}H_{18}N_3S$.⁶ Methyl Red (MR) is a commonly used monoazo dye in laboratory assays, textiles and other commercial products. The chemical formula of Methyl Red is $C_{15}H_{15}N_3O_2$.⁸

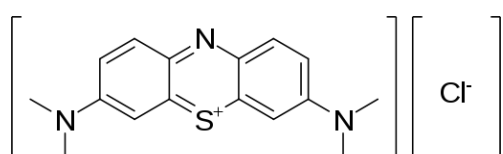


Figure 1. Molecular structure of Methylene

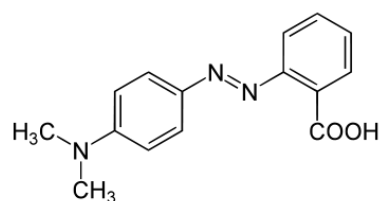


Figure 2. Molecular structure of Methyl Red Blue (MB)⁷ (MR)⁸

Industries such as petroleum refineries continuously generate large volumes of wastewater that contain high concentrations of Phenol. Phenols and Phenolic wastes from chemical and petrochemical industries at low concentration i.e. 100-1000 ppm are the major threat to the environment and aquatic life as a whole.⁹

The adsorption technique has become more popular in recent years for wastewater treatment. The term biosorption is used to describe the process that is based on biological or biomass materials. The bio-adsorbents have affinity for heavy metal ions to form metal complexes or chelates due to having functional groups including carboxyl, hydroxyl, imidazole, sulphhydryl, amino, phosphate, sulphate, thioether, phenol, carbonyl and amide etc. and chemical treatment increases the number of these functional groups.¹⁰ Paddy is one of most widely planted crop in Sri Lanka. During mauling of paddy, about 22 % of the weight of paddy is received as husk.¹¹

Modification of thermally treated rice husk with Phosphoric acid increases the surface area. The average pore diameter also increases. There is an improvement in micro-pore volume. Scanning Electron Microscope analysis has confirmed the improvement in surface area and pore development resulting from the Phosphoric acid modification while Fourier Transform Infra Red analysis has revealed the existence of Phosphorous-oxy-containing functional groups on the surface of the Phosphoric acid modified rice husk.¹²

2. EXPERIMENTAL METHODS

2.1. Collection of adsorbent and adsorbates

Rice husk used as adsorbent in this study was obtained from the local rice mill situated in Kurunegala district. In order to measure the ability of the rice husk adsorbent to treat various pollutants in industrial wastewater, two samples were obtained from industries. One is from motor vehicles cleaning and repairing industry located in Maradana area in Colombo district and the second sample from food manufacturing minor cottage industry located in Dambadeniya area in Kurunegala district.

2.2. Preparation and chemical modification of adsorbent

The particle size of rice husk obtained was 355 μm . The modification was done by chemical treatment of sieved rice husk (50 g) with H_3PO_4 (1.0 M) heated on the magnetic stirrer (at 150 rpm) at 100 $^\circ\text{C}$ until it totally formed a paste. The modified rice husk was washed with de-ionized water until pH 7. It was later dried in the oven at about 80 $^\circ\text{C}$ to remove moisture.

2.3. Experimental procedure for selected adsorbates by chemically modified rice husk

The experimental procedure was carried out by shaking of modified rice husk of different adsorbent dosages 0.5, 1, 1.5, 2, 2.5 g with 50 mL aqueous solution of CdCl_2 , CuSO_4 , Methyl Red, Methylene Blue and Phenol with different initial concentrations at room temperature and at different pHs 2, 4, 6, 8, 10 in different conical flasks in an orbital shaker at a constant speed of 120 rpm with different contact time of 30, 60, 100, 140, 180 minutes. The pH of the adsorbate solutions were adjusted by manually adding HCl (0.1 M) or NaOH (0.1 M) solutions using a pH meter. After the equilibrium has attained, adsorbent and adsorbate were separated by filtration.

2.4. Determination of equilibrium concentrations of selected adsorbates

The equilibrium concentration of Cd(II) was estimated through Atomic Absorption Spectrophotometer using a SensAA Acetylene fuel atomic absorption spectrophotometer. A UV-Vis spectrophotometer (BIOBASE BK-D580) was used for the analysis of Copper solutions complexed with Ammonia (7.5 N).¹³ A calibration curve was obtained by plotting the absorbance against concentration of the standard Cu(II) solution at a wavelength of 610 nm.^{13,14,15} The residual concentrations of Methyl Red was measured at 450 nm¹⁶ and Methylene Blue at 665 nm^{17, 18, 19} using an UV-Visible spectrophotometer (BIOBASE BK-D580). For the analysis of Phenol concentration, a calibration curve was obtained by plotting the absorbance against concentration of the standard Phenol solution at a wavelength of 710 nm.^{20, 21}

2.5. Calculation of removal percentage and adsorption capacity for the adsorbates

$$\text{Removal percentage (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

C_0 - initial concentration of the adsorbate in the solution

C_e - equilibrium concentration of adsorbate in the solution

The adsorption capacity q_e of all the adsorbates were calculated using the equation (2)¹⁶,

$$q_e = \frac{v}{w} (C_0 - C_e) \quad (2)$$

where,

q_e - amount of adsorbate adsorbed at equilibrium per unit weight of sorbent (mg/g)

v - volume of the solution (L)

w - amount of sorbent (g)

2.6. Experimental procedure for industrial wastewater treatment using chemically modified rice husk

In the first sample, Cadmium was detected using Atomic Absorption Spectrophotometer (SensAA Acetylene fuel). Rice husk was used as the adsorbent to remove the trace amount of Cadmium with 0.5 g of adsorbent dosage, at neutral pH, with 50 mL of wastewater sample at 30 °C temperature. In the second sample, colour of the wastewater obtained was egg yellow. The wavelength of maximum absorption was determined using UV-Vis spectrophotometer (BIOBASE BK-D580). Then chemically modified rice husk was used as the adsorbent with 1 g of adsorbent dosage, at neutral pH with 50 mL of wastewater sample at 30 °C temperature. Finally the removal efficiency was determined for wastewater samples using the corresponding equation.

2.7. Calculation of required parameters for plotting the adsorption isotherms

Required parameters were calculated to build the adsorption isotherms for various pollutants. The parameters were calculated according to the linear forms of Langmuir, Freundlich, Temkin and Dubinin – Radushkevich adsorption isotherms and the best fitting isotherm was determined.

1. Langmuir isotherm²² $q_e = \frac{Q_m K_a C_e}{(1 + K_a C_e)}$

2. Freundlich isotherm²² $q_e = K_f C_e^{1/n}$

3. Temkin isotherm²² $q_e = \frac{RT}{b} \ln (A C_e)$

4. Dubinin–Radushkevich (D-R) isotherm²²

$$q_e = Q_m \exp (-K \varepsilon^2) \text{ where } E = \frac{1}{\sqrt{2K}}$$

Here,

q_e - equilibrium sorption concentration of solute per gram of adsorbent (mg/g)

C_e - equilibrium aqueous concentration of the solute (mg/L)

Q_m - maximum adsorption capacity

K_a - Langmuir constant

A - equilibrium binding constant corresponding to the maximum binding energy (L/g)

K_f - Freundlich constant related to the adsorption capacity

n - Freundlich constant related to intensity of adsorption

b - Temkin isotherm constant

$RT/b = B$ - Temkin constant related to heat of sorption (J/mol)

R - universal gas constant (8.314 J/mol/K)

T - absolute solution temperature (K)

K- constant related to the adsorption energy

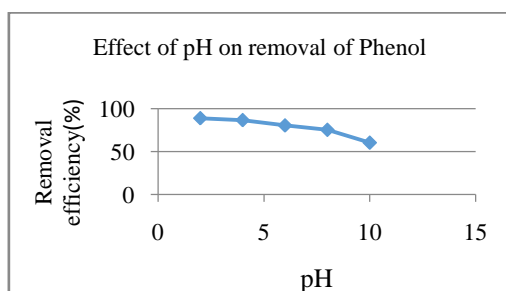
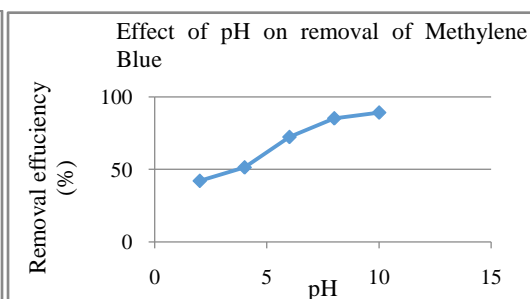
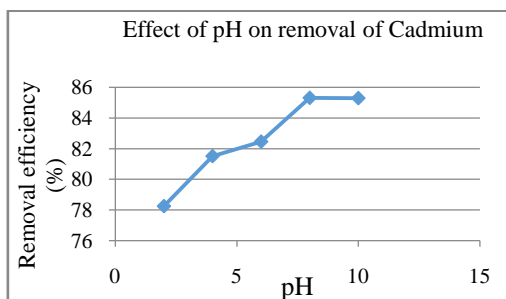
ε - potential energy of the surface

E - mean free energy (kJ/mol)

3. RESULTS AND DISCUSSION

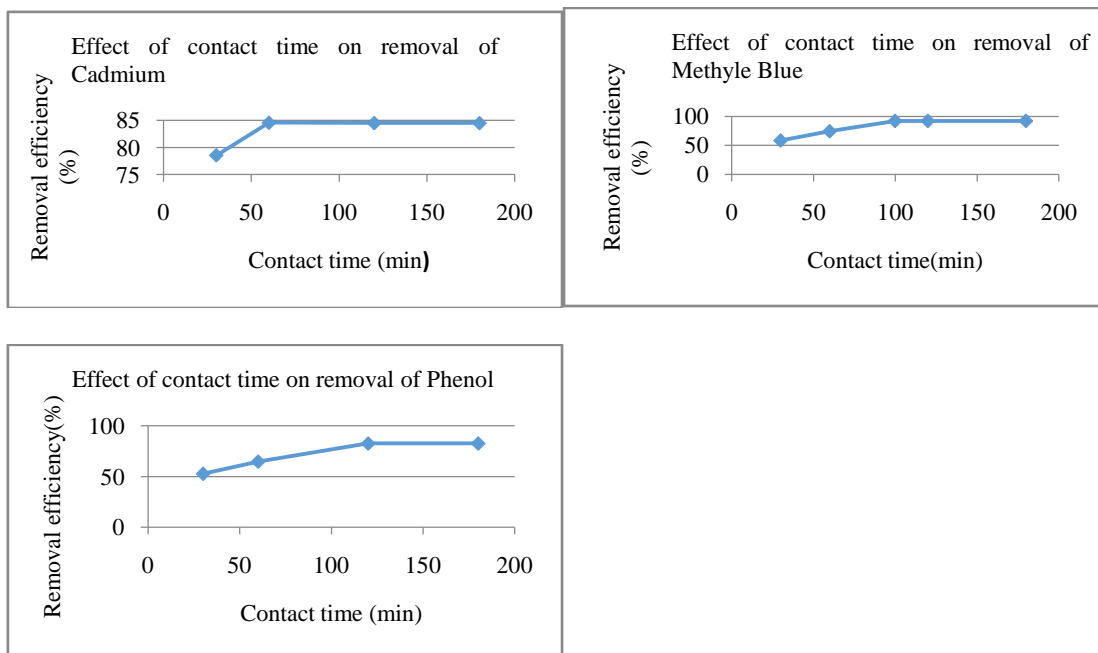
3.1. Effect of pH on removal of Cadmium, Methylene Blue and Phenol

Surface distribution mainly depends on the pH of the system.²³ The percent adsorption of metal ion decreased with decreasing pH, because protons compete with Cd metal ion for sorption sites on the adsorbent surface.²³ Maximum pH for the removal of Cd is occurred at pH = 9. This is due to the fact that precipitation of Cd starts at pH = 8.3.^{23, 24} The increasing trend of removal of Methylene Blue with increasing pH is dependent on the nature of the adsorbent. Phenol, which is a weak acid, will be adsorbed to a lesser extent at higher pH values. Phenol forms salts, which readily ionize leaving negative charge on the Phenolic group. At high pH ranges, the surface of rice husk adsorbent will be negatively charged. So there will be a repulsion between Phenoxide ion and adsorbent surface.^{25, 26} This leads to the decrease in percent of sorption.



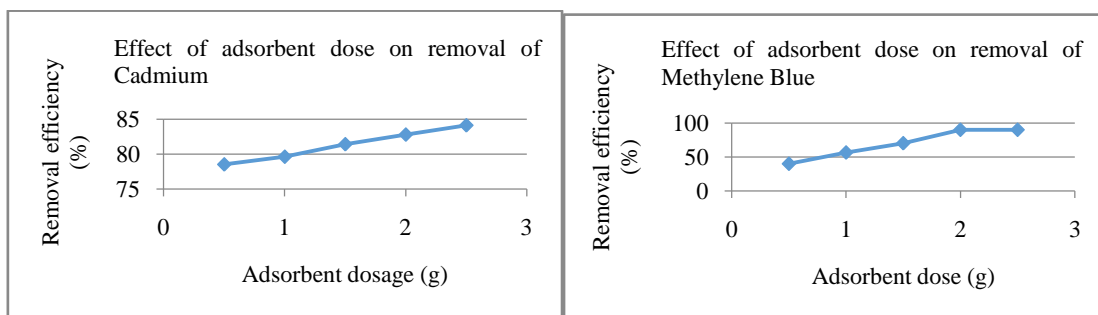
3.2. Effect of contact time on removal of Cadmium, Methylene Blue and Phenol

The sorption process can be considered very fast because of the largest amount of Cd attached to the sorbent within the first 60 minutes of adsorption. For Methylene Blue it is clear that the extent of adsorption is rapid in the initial stages and becomes slow in later stages till saturation of the adsorbent is allowed. Large number of vacant surface sites are available during the initial stage and with the passage of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between solute molecules.²⁷ Equilibrium time required for the adsorption of Phenol on rice husk is almost 180 minutes.



3.3. Effect of adsorbent dosage on removal of Cadmium, Methylene Blue and Phenol

The increase in percentage removal of Cadmium with increase in adsorbent dose was due to the availability of high external surface area, more and more sorption sites for the solutes to adsorb. Similar results were obtained for Methylene Blue and Phenol adsorption also.



3.4. Determination of removal percentage, adsorption capacity and the best fitting isotherms of heavy metals, dyes and Phenol at neutral pH

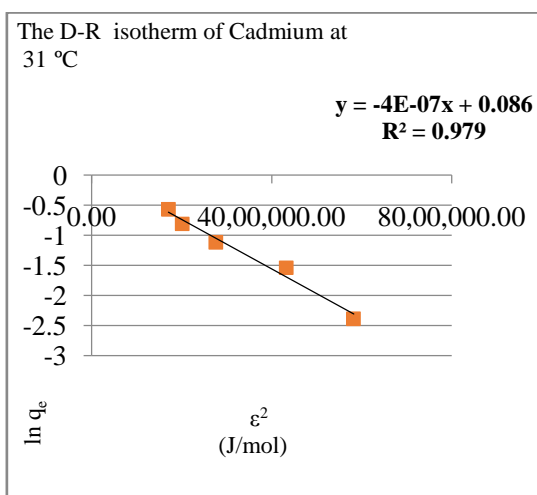
The applicability of the isotherm models to the adsorption study done was compared by judging the correlation coefficients, R^2 values. Four models, Langmuir, Freundlich, Temkin and Dubinin–Radushkevich equations were used to determine the best fitting isotherm.

3.4.1. Adsorption of Cadmium by rice husk from synthetic wastewater at 31 °C

The correlation coefficient ($R^2 = 0.979$) value is higher for Dubinin–Radushkevich isotherm. Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution on to a heterogeneous surface.²² The approach was usually applied to distinguish the physical and chemical adsorption of metal ions with its mean free energy, E per molecule of adsorbate.

Table 1. Parameters for plotting Langmuir, Freundlich, Temkin and Dubinin Radushkevich adsorption isotherms of Cadmium adsorption

C ₀ (mg/L)	C _e (mg/L)	Removal percentage (%)	1/C _e	Log C _e	Ln C _e	q _e (mg/g)	Log q _e	Ln q _e	C _e /q _e (g/L)	Σ ²
2	0.626	68.7	1.5974	-0.2034	-0.4684	0.0916	-1.0381	-2.3903	6.8341	5,819,947.58
4	0.783	80.425	1.2771	-0.1062	-0.2446	0.2145	-0.6686	-1.5394	3.6503	4,325,749.16
6	1.076	82.067	0.9294	0.0318	0.0733	0.3283	-0.4837	-1.1138	3.2775	2,759,067.45
8	1.324	83.45	0.7553	0.1219	0.2807	0.4451	-0.3515	-0.8095	2.9746	2,014,033.68
10	1.478	85.22	0.6766	0.1697	0.3907	0.5681	-0.2456	-0.5655	2.6017	1,706,130.39



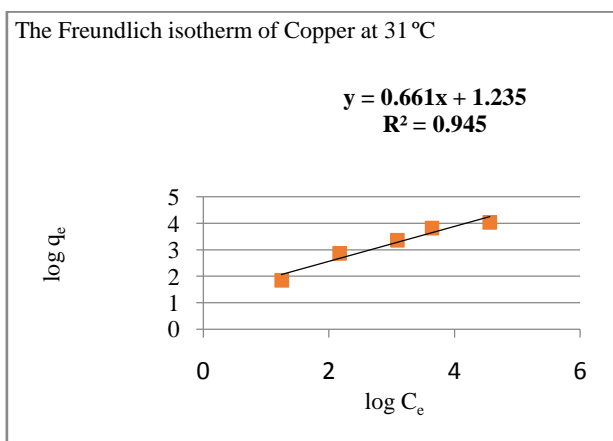
Dubinin- Radushkevich isotherm			
Q _m (mg/g)	K (mol ² /kJ ²)	E (kJ/mol)	R ²
1.0898	4 X 10 ⁻⁷	1.118	0.979

3.4.2. Adsorption of Copper by rice husk from synthetic wastewater at 31 °C

From the four isotherm models, correlation co-efficient (R²) value was higher to Freundlich model (R² = 0.945). The slope of 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero.²⁸ If value of 1/n is below one it indicates a normal adsorption. On the other hand, 1/n being above one indicates cooperative adsorption.²²

Table 2. Parameters for plotting Langmuir, Freundlich, Temkin and Dubinin Radushkevich adsorption isotherms of Copper adsorption

C ₀ (mg/L)	C _e (mg/L)	Removal percentage (%)	1/C _e	Log C _e	Ln C _e	q _e (mg/g)	Log q _e	Ln q _e	C _e /q _e (g/L)	Σ ²
25	6.302	74.792	0.158 7	0.7995	1.840 9	1.246	0.0955	0.2199	5.0578	138,603.023
50	17.473	65.054	0.057 2	1.2424	2.860 7	2.168	0.3361	0.7738	8.0595	19,747.712
75	28.643	61.809	0.034 9	1.457	3.354 9	3.09	0.4899	1.1282	9.2696	7,515.458
100	45.399	54.601	0.022 0	1.657	3.815 5	3.64	0.5611	1.292	12.472 3	3,035.849
125	56.569	54.745	0.017 7	1.7526	4.035 5	4.562	0.6592	1.5178	12.4	1956.335



Freundlich isotherm			
1/n	n	K _f (mg/g)	R ²
0.661	1.513	17.179	0.945

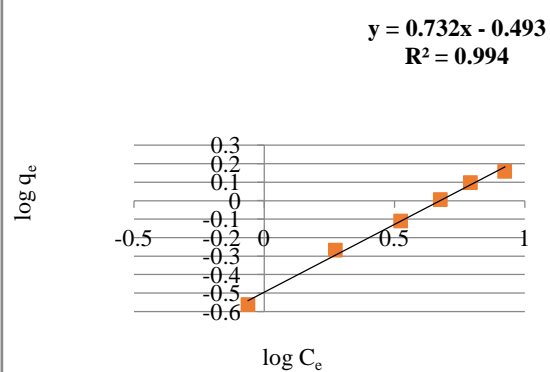
3.4.3. Adsorption of Methyl Red by rice husk from synthetic wastewater at 31 °C

A high regression correlation coefficient, R² (0.994) was shown by the Freundlich model. The K_f value and 1/n value was recorded at 3.112 (mg/g) and 0.732, respectively. If n lies between one and ten, this indicates a favourable sorption process.²²

Table 3. Parameters for plotting Langmuir, Freundlich, Temkin and Dubinin Radushkevich adsorption isotherms of Methyl red adsorption

C ₀ (mg/L)	C _e (mg/L)	Removal percentage (%)	1/C _e	Log C _e	Ln C _e	q _e (mg/g)	Log q _e	Ln q _e	C _e /q _e (g/L)	Σ ²
5	0.865	82.7	1.1561	-0.0630	-0.1450	0.275	-0.5607	-1.291	3.1455	3745993.02
10	1.878	81.22	0.5325	0.2737	0.6302	0.541	-0.2668	-0.6143	3.4713	1156531.83
15	3.343	77.713	0.2991	0.5241	1.2069	0.777	-0.1096	-0.2523	4.3024	434623.088
20	4.75	76.25	0.2105	0.6767	1.5581	1.016	0.0069	0.0159	4.6752	231511.193
25	6.196	75.216	0.1614	0.7921	1.8239	1.254	0.0983	0.2263	4.9410	142026.173
30	8.392	72.027	0.1192	0.9239	2.1273	1.441	0.1587	0.3653	5.8237	80460.386

The Freundlich isotherm of Methyl Red at 31 °C



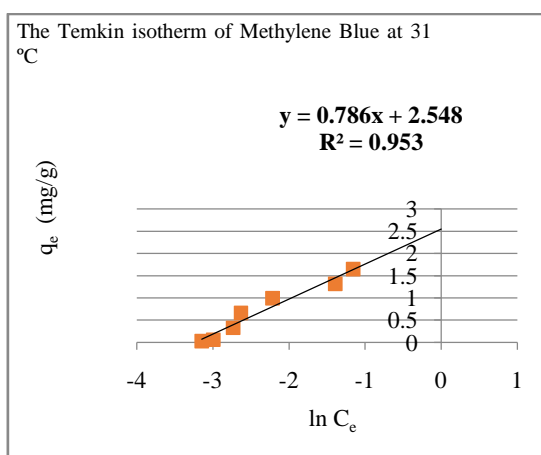
Freundlich isotherm			
1/n	n	K _f (mg/g)	R ²
0.732	1.366	3.112	0.994

3.4.4. Adsorption of Methylene Blue by rice husk from synthetic wastewater at 31 °C

The regression coefficient is higher for Temkin isotherm. (R² = 0.953). This isotherm contains a factor that explicitly taking into account of adsorbent-adsorbate interactions.²²

Table 4. Parameters for plotting Langmuir, Freundlich, Temkin and DubininRadushkevich adsorption isotherms of Methylene Blue adsorption

C ₀ (mg/L)	C _e (mg/L)	Removal percentage (%)	1/C _e	Log C _e	Ln C _e	q _e (mg/g)	Log q _e	Ln q _e	C _e /q _e (g/L)	Σ ²
0.5	0.043	91.4	23.256	-1.3665	-3.1466	0.03	-1.5228	-3.5066	1.4333	64952298.759
1	0.05	95	20	-1.3010	-2.9957	0.063	-1.2007	-2.7646	0.7937	59210559.424
5	0.065	98.7	15.385	-1.1871	-2.7334	0.329	-0.4828	-1.1117	0.1976	49949912.634
10	0.072	99.28	13.889	-1.1427	-2.6311	0.662	-0.1791	-0.4125	0.1088	46568766.63
15	0.109	99.273	9.174	-0.9626	-2.2164	0.993	-0.0031	-0.007	0.1098	34379989.31
20	0.248	98.76	4.032	-0.6055	-1.3943	1.317	0.1195	0.2754	0.1883	16679471.49
25	0.314	98.744	3.185	-0.5031	-1.1584	1.646	0.2164	0.4983	0.1908	13088480.59



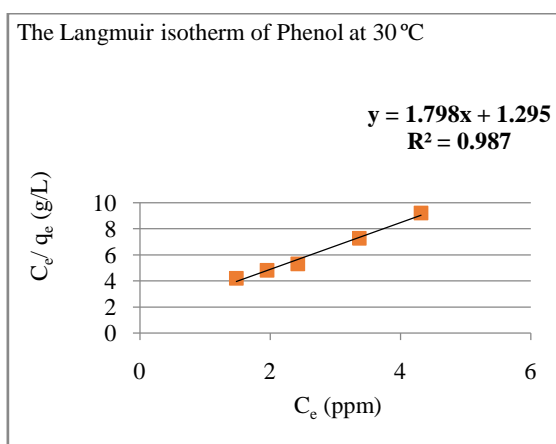
Temkin isotherm			
A (L/g)	b	B (J/mol)	R ²
25.585	3215.593	0.786	0.953

3.4.5. Adsorption of Phenol by rice husk from synthetic wastewater at 31 °C

The results reveal that the adsorption of Phenol on rice husk obeys the Langmuir adsorption isotherm. From the Langmuir model, the magnitude of Q_m = 0.556 indicates that the amount of Phenol per unit weight of sorbent to form a complete monolayer on the surface appears to be significantly high for Phenol– rice husk system.

Table 5. Parameters for plotting Langmuir, Freundlich, Temkin and Dubinin Radushkevich adsorption isotherms of Phenol adsorption

C ₀ (mg/L)	C _e (mg/L)	Removal percentage (%)	1/C _e	Log C _e	Ln C _e	q _e (mg/g)	Log q _e	Ln q _e	C _e /q _e (g/L)	Σ ²
5	1.48	70.4	0.6757	0.1703	0.3920	0.352	-0.4535	-1.0441	4.2045	1690991.006
6	1.953	67.45	0.512	0.2907	0.6694	0.405	-0.3925	-0.9039	4.8222	1082968.157
7	2.425	65.357	0.4124	0.3847	0.8858	0.457	-0.3401	-0.783	5.3063	756655.954
8	3.371	57.863	0.2966	0.5278	1.2152	0.463	-0.3344	-0.77	7.2808	428005.349
9	4.317	52.03	0.2316	0.6352	1.4626	0.468	-0.3298	-0.7593	9.2244	275349.212



Langmuir isotherm		
Q _m (mg/g)	K _a (L/mg)	R ²
0.556	1.389	0.987

3.5. Application of rice husk for the removal of pollutants in industrial wastewater

In the first wastewater sample which was obtained from motor cleaning and repairing industry located at Colombo district, the amount of Cadmium detected was 0.01 ppm. The removal efficiency was found to be 72.37 %. In the second sample, colour of the wastewater obtained was egg yellow. This wastewater sample showed maximum of absorption at wavelength of 520 nm using UV-Visible spectrophotometer (BIOBASE BK-D580) and the amount of dye particle detected in the wastewater sample was 27.92 ppm. It was determined that the dye particle contains Carmoisine E122 which is also known as Azorubine. It falls under azo dye group and has the ability to cause increased hyper activity in children.²⁹Rice husk was able to remove 83.42 % of the dye material from the wastewater. Therefore, it is clearly seen that rice husk has a greater tendency to remove metal ions and dyes.

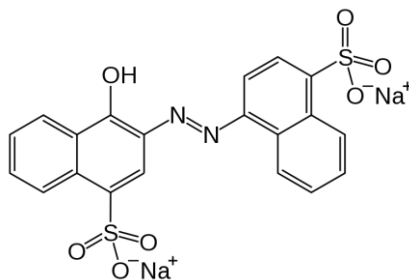


Figure 3. Molecular structure of Carmoisine E122²⁹

4. CONCLUSION

Through this research study, the main conclusions that can be drawn from the current investigation are given below:

- Concerning the adsorption process, the result showed that the rice husk is an environmental friendly green adsorbent and its effectiveness can be improved through chemical activation with Phosphoric acid. The prepared adsorbent was shown to be effective in removing organic pollutants especially dyes (Methyl Red and Methylene Blue), Phenol and toxic heavy metals (Cadmium and Copper).
- The effect of initial pH, adsorbent dosage, contact time and initial concentration of the solution showed that the parameters react differently towards the heavy metals, dyes and Phenol. Indeed, pH variation affects the adsorption much than other factors. The removal efficiency is higher for Phenol and azo dyes (Methyl Red) at low pH values. And it is shown that the removal efficiency is higher for heavy metals and cationic dyes (Methylene Blue) at higher pH values.
- □ Several isotherm models such as Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) were employed to understand the sorption behaviour. In each case, different models allowed the best fit for the contaminants considered. Respective isotherm constants were calculated to describe the adsorption process.

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