IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736. Volume 17, Issue 11 Ser. 1 (November 2024), PP 36-47
www.iosrjournals.org

Removal Of Phenolic Compounds From Aqueous Media Using Triethylamine Anchored Rice Husks

Kuria M. Serah, Isaac W. Mwangi, Peter W. Njoroge
(Department Of Chemistry, Kenyatta University, P.O Box 43844-0100, Nairobi, Kenya)
(Department Of Physical And Biological Sciences, Murang'a University Of Technology, P.O Box 75-10200, Murang'a, Kenya)

Abstract

Phenolic compounds in water are contaminants of concern even at low concentrations. They get incorporated in water from various sources such as industrial, mining and natural sources. Natural sources of phenolic compounds are plant saplings and aquatic plants such as green and red marine algae. This makes these compounds readily available from both natural and industrial sources to pollute the water. Phenolic compounds take long to diminish and are carcinogenic. Phenolic compounds in water affects its taste and oduor of the vital products. They equally affect the taste and odour of marine organisms in that water as well as the animals that consume it. To minimize the negative effects from these pollutants, their elimination is the only option. This paper gives an account on the preparation and modification of rice husks with triethylamine and how it is used on the elimination of phenolic compounds from water by adsorption. Modification was carried out by chlorinating and anchoring with an amino group on the rice husks to form a quaternary ammonium compound. The existence of the functional groups that performed as the binding sites was confirmed by Fourier Transform Infrared (FT-IR) analysis. The anchoring of the amino group was confirmed by the occurrence of a signal at 3424.67cm-1. The carbon skeleton of the modified product resembled that of cellulose by solid-state 13C NMR. Change of resonance frequencies in the modified material confirmed the chlorination and subsequent the anchoring of ethylene diamine within the cellulose structure. Scanning electron microscopy analysis displayed an increase in the porosity of the modified material as related to the parent material. The material was then applied for sorption experiments and it was confirmed that the optimum pH was of 5.5 for all the phenolic compounds under study. There was over 90% phenolic compounds uptake in the first 2 min of contact time. The adsorption followed the Langmuir monolayer adsorption model with correlation coefficient (R2) of 0.9895 for Naphthol. The elimination of Naphthol with modified rice husks gave the best adsorption capacity of 0.6125 mg/g. Thus modified rice husks is an effective adsorbent material for eradication of phenolic substances originating from unsafe drinking water

Keywords: *Adsorption, Adsorption Isotherms, Adsorbents, sorbate*

Date of Submission: 10-11-2024 Date of Acceptance: 20-11-2024

I. Introduction

Phenols are aromatic organic compounds that have moieties basically one or more hydroxyl (-OH) groups in their cellular structure capable of forming bonds with either organic or inorganic compounds (Song *et al.*, 2016). Their chemical structural influence their solubility in variety of solvents either polar or not as well as chemical and physical properties. The partial loss of oxygen's negative charge to the ring and the charge delocalization result from the conjugation of oxygen atom electron pairs with aromatic structure. As a result, the O-H bond polarizes, forming a phenolate ion that gives the molecule its acidic properties (Soto-Hernández *et al.*, 2017). The phenolic compounds are fairly soluble in water due to the interaction between the delocalized electrons of the ring and one of the lone pairs on the oxygen atom, which allows the compound to establish hydrogen bonds with the water. Owing to such characteristic, water and phenolic compounds from the surroundings interact to disperse the latter uniformly in that all-purpose solvent.

Phenolic compounds can be found from a vast range of sources phenolic compounds in our natural environment. This might include industrial or natural sources (Gharaati, 2019). The natural sources are mainly plants from cultured and natural sources and provide valuable protective and health-promoting extracts (Nurzyńska, 2023). They are generally found in high concentrations in the plant saplings some aquatic plants such as green and red marine algae. That being the case, phenolic compounds from the environment can easily get incorporated and be dispersed in water. Phenolic compounds take long time to degrade in the environment and are carcinogenic (Gharaati, 2019). Consuming waters harboring such compounds even at low concentrations is unsafe and may lead to serious health risks to humans, animals, and aquatic systems (Gharaati, 2019; Chua *et al.*, 1992; Schumacher *et al*., 2020). Their health effects can be both severe and long-term (Quimbo et al., 2015). Phenols exist in common byproducts such as Bisphenol a (BPA), chlorophenols (CPs), and phenolic endocrine disrupting compounds. Studies have shown that the phenolic compounds cause fetal body weight loss, growth deferment, and abnormal development in the offspring. Thus, there is a need for the removal of phenolic compounds in waters that interact with animals. Phenolic compounds create stable complexes when they interact with quaternary ammonium compounds (Jin *et al*., 1991). Quaternary ammonium salts are ionic surface active chemical agent s that are typically composed of a single nitrogen atom and are surrounded on all four of its sites (R4N+) by carbon atom replacements (Wang *et al.*, 2013).

These cations interact to establish strong connections with any neutral or negatively charged material because they are permanently charged (Wang *et al*., 2013). Because of their chemical interaction with the lignocellulosic substrates in the wood, quaternary ammonium compounds have been used as a desirable material for wood preservation (Jin and Preston, 1991). In an effort to provide solutions, this reaction aids in the removal of phenolic chemicals from water.

This study reports discusses the production of rice husks that have been chemically altered using triethylamine, and how to use them to remove phenolic chemicals from water. Diluted hydrochloric acid can be used to quickly remove the adsorbed phenolic chemicals from the adsorbent.

II. Materials And Methods

Sampling and Preparation

Rice husks were collected from Mwea rice millers in Kirinyaga County, Kenya. The rice husks was packed into ten kilogram bags and sent to the Kenyatta University laboratory, where it was cleaned with distilled water and dried at sixty degrees Celsius in an oven. Before the test, the dried rice husks were ground and passed into a powder of mesh filter (150–250 mm), and kept in an airtight bottle.

A sample, 20 g, of crushed husk was chemically modified with triethylamine in accordance with Mwangi *et al.* (2012).

Figure I shows a picture of a sample of rice husks, RH.

Figure 1: **The sample of raw rice husks (RH)**

Chemicals and reagents

Phenol model solutions were prepared in 0.1 mol L -1 sodium acetate solution to retain constant ionic strength and stored in plastic containers. Water samples were collected from designated fish ponds within Kiambu and kept in plastic bottles and secured in dark environment. All the stock solutions were prepared in double distilled water and all reagents were of analytical grade. The phenolic compound solutions in this study were: 1-naphthol, 4-nitrophenol, anthracene and resorcinol. These phenol stock standard solutions (1000 µg/l) model solutions were prepared in 0.1 mol L -1 sodium acetate solution to maintain constant ionic strength and stored in plastic containers. Other reagents included: thionylchloride, hydrochloric acid, ethanol, sodium acetate, sodium hydroxide.

Instrumentation

A Shimadzu UV-2450 UV Vis spectrophotometer (Specord 200, manufactured in Germany) was used to measure the amount of phenolic ions present in aqueous solutions. To identify the functional groups in the modified adsorbent, the adsorbent was characterized using an ATR mode on a Fourier transform infrared (FT-IR) spectrophotometer (IR 100 by Shimadzu) (Mukamel, 2000).

Using a 13C solid state NMR apparatus with a cross polarization/magic angle spinning (CP/MAS) capability (Bruker Avance 600 spectrometer, Hanau, Germany), the sorbent material was studied.

Preparation of the sorbent material

Modification of the Rice Husks

A three-neck flask with 200 ml of aniline and 30 ml of thionyl chloride was filled with a sample of 20 g of the dried and crushed rice husks that had been previously activated at 80 ^{0} C for 12 hours. The mixture was then mechanically stirred and dropped-wise added to. For five hours, the mixture was agitated at roughly 60˚C. After filtering, washing, and drying at 70˚C for 12 hours, the product was finished. Next, 200 milliliters of ethanol and a 10-gram sample of the chlorinated substance were added to a flask with three necks. 100 milliliters of triethylamine were added to the resultant liquid and stirred. To produce a modified substance, the mixture was refluxed at 80˚C for 12 hours while being continuously stirred. Next, the substance was applied to actual water as an adsorbent.

Batch experiments

For the batch adsorption tests, a temperature-controlled water-bath shaker (DKZ-1 NO.1007827) was utilized. The trials were conducted at the same rate of vibration. Twenty milliliters of aqueous phenolate ions were added to 100 milliliter plastic bottles containing known masses of both modified and unmodified rice husks for every experimental run.

These bottles were centrifuged and filtered after being shaken continuously at 170 rpm and 25 °C. Using UV-vis spectroscopy, the amount of phenolate ions in the produced filtrates was determined. Equations 1 and 2 were used to determine the percentage of phenols ions eliminated as well as the amount of phenolate ions adsorbed per unit mass of adsorbed.

Equation

$$q_e = \frac{(c_o - c_e)v}{m} \qquad (1)$$

$$R = 100\left(\frac{c_o - c_e}{c_o}\right) \qquad (2)$$

Where,
qe = phenolate ion adsorbed per unit mass of adsorbed at equilibrium.
co = Initial concentration of sorbate.
ce = Concentration of sorbate at equilibrium.
m = mass of sorbate (atomic mass).
v = volume of solution,

Optimization experiments

Four parameters of the experiment were optimized. These included adsorption capacity, pH, contact time, and the impact of sorbent dose in order to determine the ideal experimental conditions. The modified material was subsequently used to subtract specific phenolic chemicals from real polluted water samples, as well as from model aqueous solutions including 1-naphthol, 4 Nitrophenol, anthracene, and resorcinol.

Effect of pH on adsorption of phenols.

By using model solutions buffered at different pH levels and batch adsorption, the ideal pH values were found. The 0.03 g quaternized substance was weighed into 100 mL polythene screw cap bottles in batches. In a buffer solution, 20 milliliters of phenolic model solutions (30 mg L-1) were made and brought to the appropriate pH levels of 3 and 9.

After an hour of equilibration, the mixes' phenolic ion content was determined using UV-Vis spectroscopy.

Effect of contact time on sorption.

By combining 20 mL of analyte solution with a concentration of 20 mg/L with 0.03 g of sorbent material each, the degree of adsorption of the phenolic ions was investigated. The combinations were buffered to the pH that each phenol responds to best. Subsequently, the mixes were allowed to acclimate in 100 mL polyethylene screw-cap bottles for pre-arranged durations ranging from 1 to 150 minutes.

Determination of adsorption capacity of phenols on cationized rice husks material.

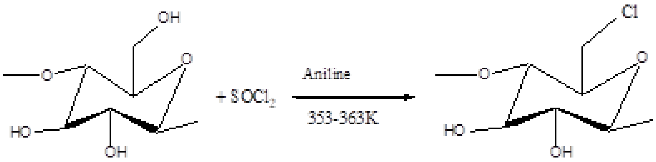
By adjusting the starting phenolic ion concentrations in batches of 20 mL of model solutions using around 0.03 g of the cationized material, the adsorption capacity was determined.

For every phenolic component, the model solutions' pH was adjusted to its ideal level. The mixtures were put on a mechanical shaker for thirty minutes, after which they were sieved and the amount of phenol was measured using UV-Vis spectroscopy.

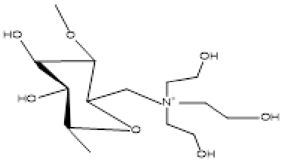
FTIR characterization

The parent material (rice husks) is essentially cellulose in nature and can be degraded by bacterial action under wet conditions (Edor *et. al*., 2018). This means that it is not very suitable for use as an adsorbent for the deduction of pollutants in its natural form. However, it contains functional groups that can be modified to stop bacterial infestation (Tianyu *et. al*., 2019).Chemically anchored functional groups can then be exploited for attachment of pollutants of interest and eliminate them from water.

An adsorbent capable for the elimination of phenolic contaminants was then synthesized by treating the parent activated dry rice husks sample material with thionylchloride and cationized with a tertiary amine. The reaction scheme for the modification process is as shown in schemes 1 and 2 respectively.



Scheme 1: Chlorination of cellulose with Thionylchloride



Scheme 2: Quaternary amine cellulose

III. Results And Discussions

FTIR was used to characterize the materials that were obtained, and the results are shown in the corresponding sections. Fourier transform infrared (FTIR) spectroscopy was used to evaluate the parent, chlorinated, and cationized adsorbents; the results are shown in Figure 1.

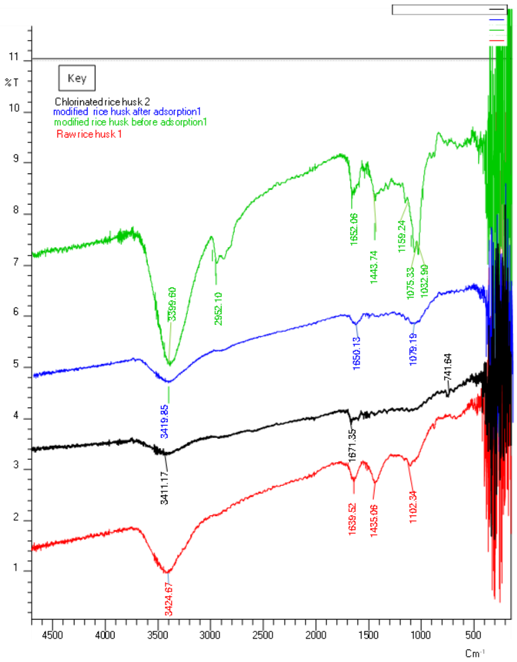


Figure.2: FTIR spectrum of the parent material and modified forms of rice husks

Results in Figure 2, show a broad peak at 3424.67 cm−1 which was likely to represent the stretching vibration of the hydroxyl group (Salih, 2012). This peak includes also inter- and hydrogen bond vibrations within individual molecules of cellulose. According to Edebali (2019), the band at 1639.52 cm−1 was attributed to the CH stretching vibration of every hydrocarbon component in polysaccharides. The vibrations of CH2 and CH bonds originating from cellulose may be the cause of a peak observed at 1435.06 cm− (Jawaid *et al*., 2020). C-H bending is responsible for the peak at 1102.34 cm- 1 (Hodson *et al*., 2020).

The absence of a carbonyl functional group in the changed material accounts for the band at 1435.06 cm-1 that was previously suggested in unmodified rice husk. This is due to -CH2 had disappeared in chlorinated rice husk. This could be due to formation of C- Cl bond (Fredricks *et al*., 1970). Formation of C- Cl bond was confirmed the new peak at 741.64 cm-1 (Bray, 1929). The thonyl chloride modified was treated with triethylamine in presence of ethanol and the results showed loss of the C-Cl peak at 741.64 cm-1 in thionyl chloride treated rice husk and formation of a new peak at 1032.90 confirmed formation of C-N bond (Taillefer *et al.*, 2013).

The results obtained confirmed a successful modification of rice husks and then the product was applied for sorption experiments.

NMR Characterization

Representation using carbon-13 NMR and the results are in figure 4.3

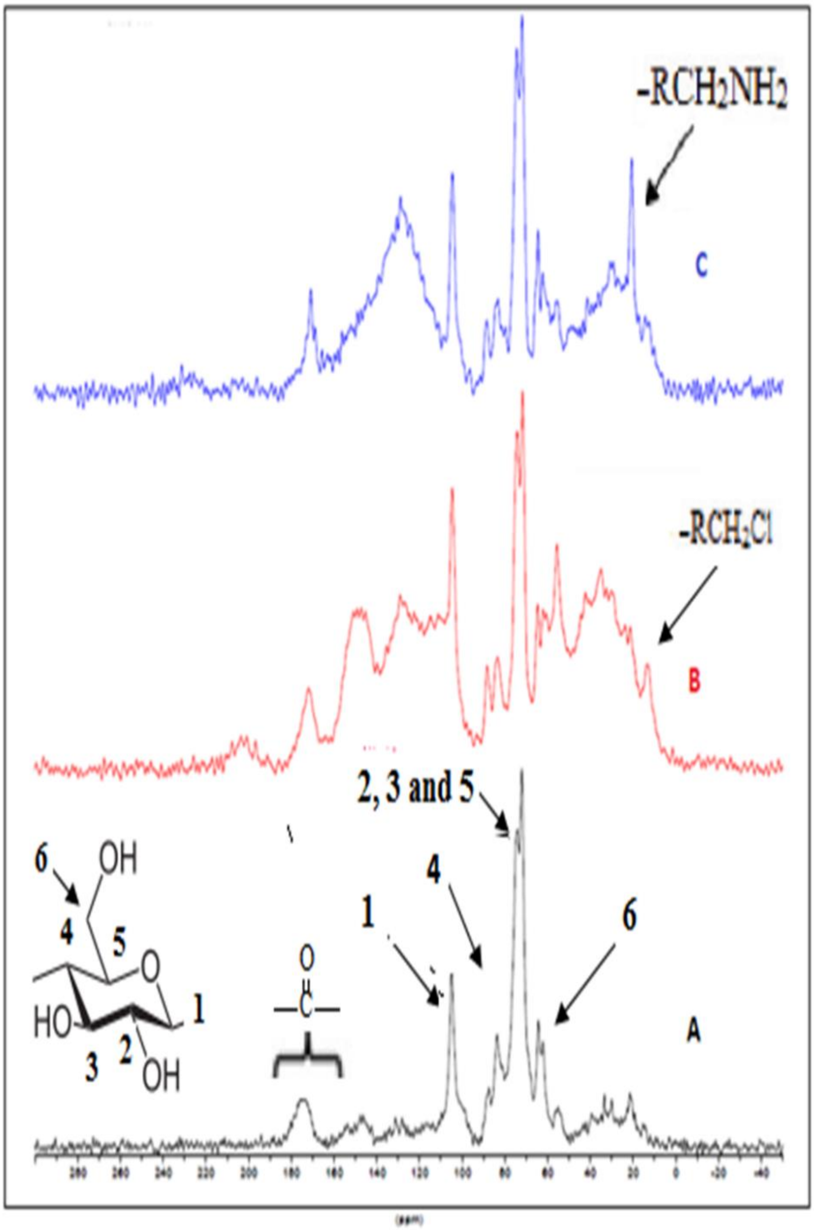


Figure.3 NMR spectrum of (A) parent (B) chlorinated (C) modified material

The spectra (A) indicates that the parent sorbent material has six carbon atoms a structure closely similar to that of cellulose (Grushka & Grinberg, 2012).The signals were assigned to respective carbon atoms at position similar to the cellulose structure in the inset. The crbon atom position 6 (C6) was most likely to be the cause of the signal between 60 and 70 δ. The the set of signals between 70 and 80 δ were likely to be assigned to C2, C3, and C5 According to Koch, Raiker, and Sternberg (2000), the signals between 81 and 93 δ were assigned to C4, and the signal between 96 and 108 δ were assigned to the C1 atom. The signal assigned to the carbonyl group (–CO) was likely to be as a result of the minor peak at approximately 172 δ (Tavares *et al*. 2004). Following chlorination, a new broad signal was found at 40–45 δ (B), which was likely to be as a result of the presence of a chlorinated carbon atom within the chlorine modified cellulose structure> The results also show that there was an amplification of signals slightly below 172 δ assigned to –CO.. A sharp signal observed at 40 δ in spectra (C) was allocated to new carbon skeleton due to a successful modification. Hence an effective functionalization of the rice husks with an amine group. This confirms the presence of each respective substitution of the desired atom or functional group in the structure of the cellulose material was successful.

Optimization experiments

To find the best parameters for the greatest amount of phenol removal from aqueous solution, optimization experiments were conducted.

Effect of pH

The pH may have an impact on the nitrogen atoms and other functional groups present in the adsorbent according to (Saitoh *et al.*, 2011) This is because charge adsorbents' surface characteristics are affected by pH. The positively charged sites decrease while the negatively charged sites grow when the pH of the adsorbent-adsorbate system rises. This study examined the effects of pH on phenol sorption ((张 & Li, 2023), with the findings shown in figure 4.2.1.

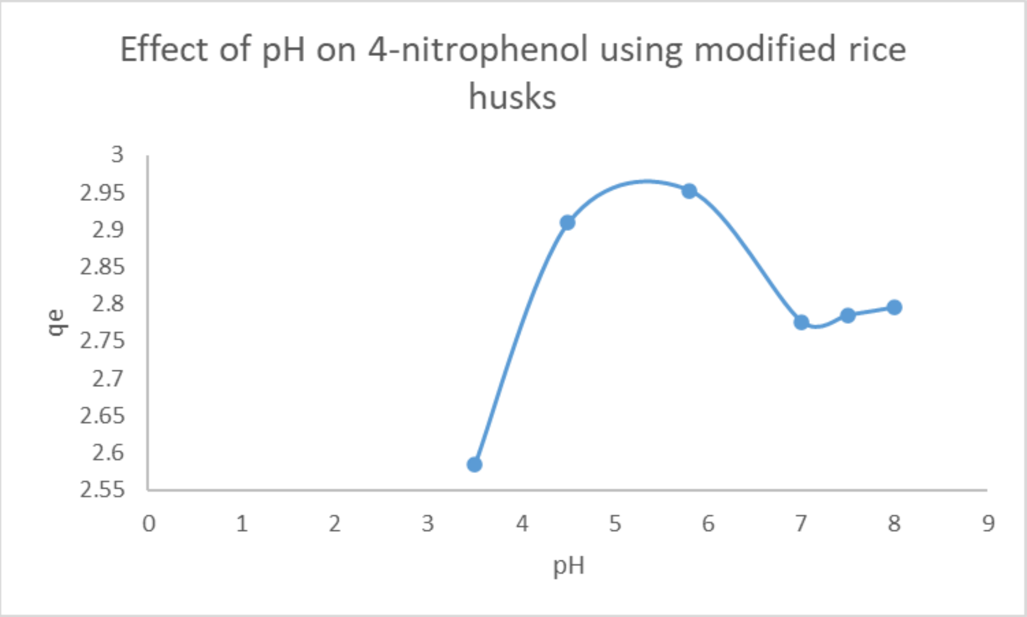


Figure 4: Effect of pH on modified rice husks (pH 3-9, temperature 273K, mass 1.0g, contact time 30minutes, and shaking speed 170 rpm)

Based on the data shown in Figure 4, it is clear that the ideal pH range for the other phenols was between 5.5 and 7.0. This is consistent with findings reported by Singh and colleagues (2006) who investigated 4-nitrophenol adsorption using a clay and Cocos nucifera shell composition.

According to other research, phenol ionization to form phenolate ions and the presence of hydroxyl ions on the adsorbent directly inhibited the adsorption of phenolate ions, which is why the adsorption of phenol from aqueous solutions decreased as the pH of the solution increased (Nagda *et al.,* 2007). At pH >7 there could be competition between negatively charged phenolate ions with hydroxide creating diffusion resistance which hinders adsorption of phenolate ion (Bonilla-Petriciolet *et al.*, 2017). A similar observation was noted in this study showing a maximum adsorption at a range between 5.5-6.5. This is as reported by Nagda *et al.*, (2007) who observed a maximum adsorption at pH values below 7.0. At extremely low pH values (<3), the formation of hydrogenphenollate takes place (Soto-Hernández *et al*., 2017) due to increased H^+ ion on the surface of the adsorbent Crini &jt Badot, 2010,)

Effect of contact time

According to Demirbasa *et al.* (2004), the rate of phenol uptake is influenced by the phenol's activity and the sorbent binding sites' capacity to store the phenol. This relationship regulates the sorbate's residence time at the solid–solution interface. Figure 3 displays the data for the sorption of 4-nitrophenol, anthracene, and resorcinol on the modified and unmodified sorbents used in this investigation.

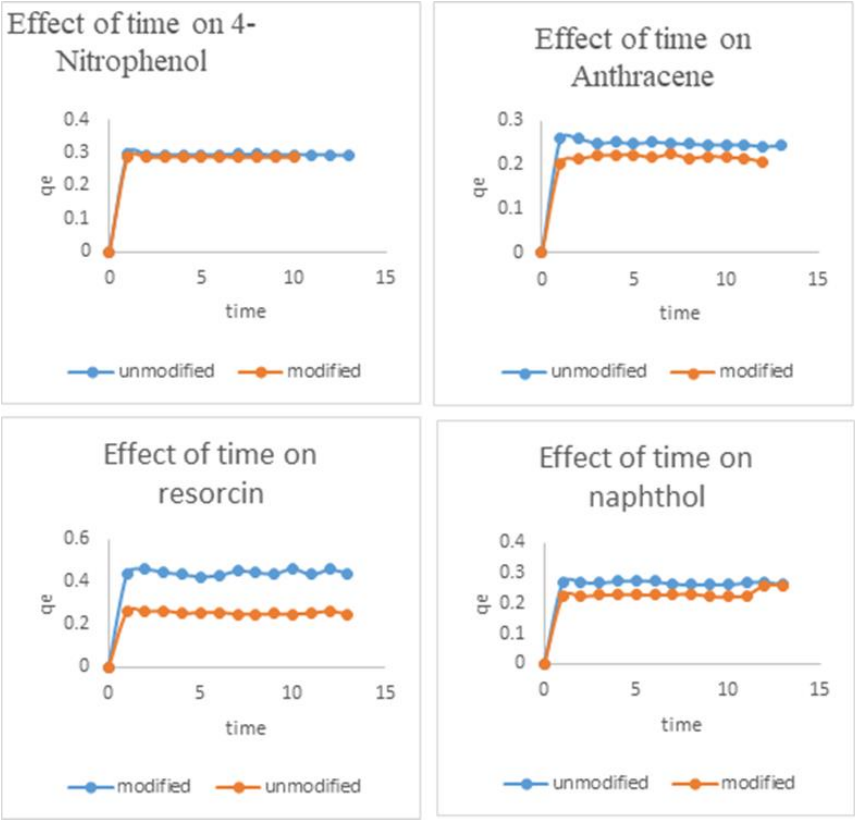


Figure 5: Effect of contact time

The general observation in Figure 4 for all the phenols showed that the overall uptake followed within 2 minutes, after which a slower uptake rate come up to a steady state. The initial speedy rate (within the first 2 min) was due to a physical sorption or ion exchange at cell surface and the following slower phase may be due to other mechanisms such as complexation, micro-precipitation.

Effect of concentration

To study the effect of concentration of both modified and unmodified rice husks, 20 ml model solutions of concentrations between 5ppm-30ppm were transferred into 100 ml polystyrene screw-cap bottles holding almost 0.01 g of the adsorbent and placed on a mechanical shaker for 30 min.
The mixture was sieved and the resultant solution analysed.

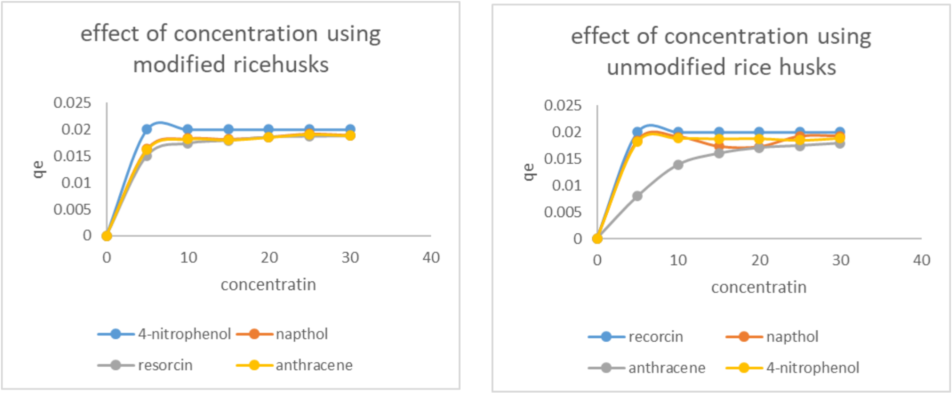


Figure 6.

The results show the variation of qe against the concentration of model solutions. Due to an availability, of binding sites, the sorption profile gave a linear pattern of the phenolic compound uptake from 0 to 5 ppm. This was followed by a plateau as the concentration increased.

According to Benhima *et al.* (2008), this can be the consequence of binding site saturation leading to a stable state. According to According to Ilhan *et al.* (2004), this could be explained the fact that concentration is what propels the phenols to occupy available adsorption sites.

Effect of sorbent dose

Separate columns were filled with varying masses (0.21.4 g) of both modified and unmodified rice husks. The pH of 100 ml of model solutions with a 10-ppm concentration was adjusted to its ideal value before they were placed onto the column at a flow rate of 3 ml min-1. The findings of the mass of the adsorbent acting against adsorption are shown in Figure 6.

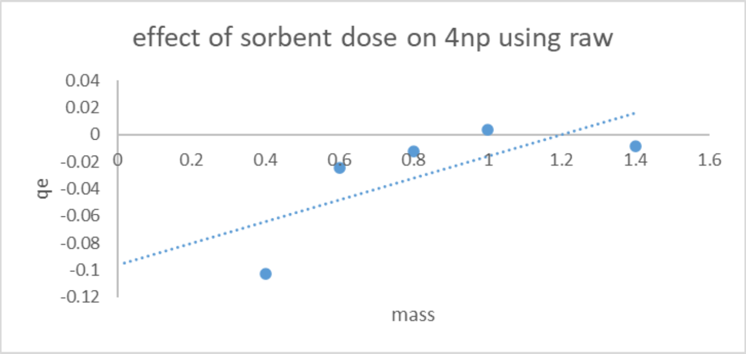
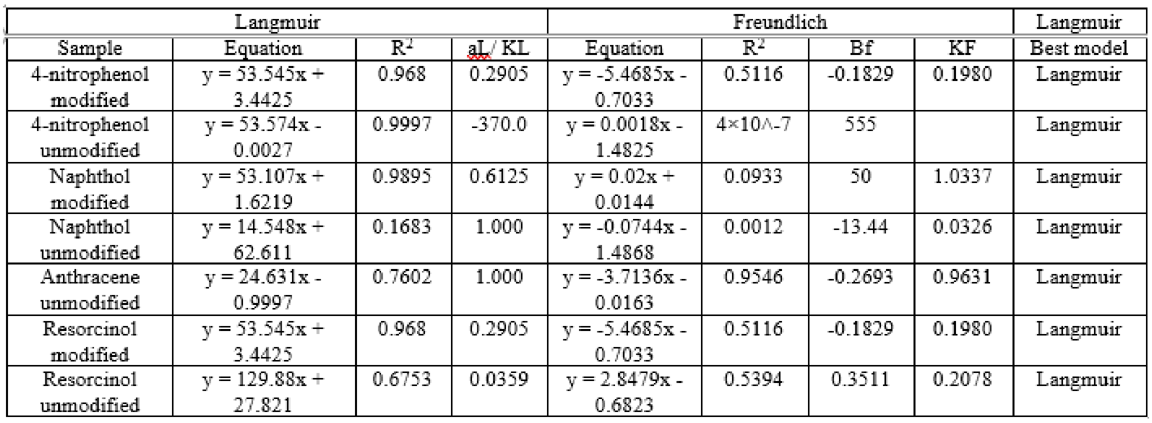


Figure 7.

Results in Figure 7 show a general observation made for all the phenols that the adsorption increased with increase in sorbate dose. Increase in mass of adsorbent contribute to more sorption due to the increased sorption sites. When most of the phenols have been adsorbed, a plateau appears as the phenol have been exhausted in solution.

Analysis of phenol sorption data: Langmuir and Freundlich isotherms

Sorbent isotherm models were utilized to ascertain the adsorption of phenolate ions, providing insight into the nature and chemical interactions involved in the adsorption process. In this work, Freundlich and Langmuir isotherm models were used to fit the data. Phenolate ion concentrations were adjusted between 5 and 30 ppm using 0.01 g of an adsorbent material and a pH of 5.5. After 30 minutes of shaking at 298 K, the mixture's findings are shown in table 3.1.



Langmuir				Freundlich				Langmuir
Sample	Equation	R^2	aL/ KL	Equation	R^2	Bf	KF	Best model
4-nitrophenol modified	y = 53.545x + 3.4425	0.968	0.2905	y = -5.4685x - 0.7033	0.5116	-0.1829	0.1980	Langmuir
4-nitrophenol unmodified	y = 53.574x - 0.0027	0.9997	-370.0	y = 0.0018x - 1.4825	4×10^-7	555		Langmuir
Naphthol modified	y = 53.107x + 1.6219	0.9895	0.6125	y = 0.02x + 0.0144	0.0933	50	1.0337	Langmuir
Naphthol unmodified	y = 14.548x + 62.611	0.1683	1.000	y = -0.0744x - 1.4868	0.0012	-13.44	0.0326	Langmuir
Anthracene unmodified	y = 24.631x - 0.9997	0.7602	1.000	y = -3.7136x - 0.0163	0.9546	-0.2693	0.9631	Langmuir
Resorcinol modified	y = 53.545x + 3.4425	0.968	0.2905	y = -5.4685x - 0.7033	0.5116	-0.1829	0.1980	Langmuir
Resorcinol unmodified	y = 129.88x + 27.821	0.6753	0.0359	y = 2.8479x - 0.6823	0.5394	0.3511	0.2078	Langmuir

Table 1: Langmuir and Freundlich isotherms results

The Langmuir model is recommended by the general observation from the values of adsorption capabilities acquired in this investigation since it had a higher R^2 value than the Freudlich model. According to Deng, Bai, and Chen (2003), the Langmuir model explains a monolayer adsorption, which suggests a chemisorption mechanism. Weak Vander Waals forces result in multi-site or physical sorption, which is confirmed by the Freundlich adsorption model.

Adsorption kinetics

To decide the mechanism of phenolate ions uptake; pseudo first order and pseudo second order rate kinetics were used. The results are presented in the table 4.4.

Table 2 Adsorption isotherms

Phenolic compounds	Pseudo-first order equation (k1)	Correlation coefficient (R^2)	Pseudo-second order equation(k2)	Correlation coefficient (R^2)	Best fit
4-nitrophenol using modified rice husks	y = 0.0609x + 1.6577	0.2881	y = 2.1188x + 2.038	0.1612	Pseudo-first order
4-nitrophenol using unmodified rice husks	y = 0.3057x + 9.3589	0.2425	y = 3.0491x - 0.148	0.2575	Pseudo-second order
resorcinol using modified rice husks	y = 0.0661x + 1.585	0.2728	y = 2.2442x + 0.0359	0.2713	Pseudo-first order
resorcinol using unmodified rice husks	y = 0.0721x + 1.7524	0.2679	y = 2.9511x - 0.2112	0.2857	Pseudo-second order
Naphthol using modified rice husks	y = 0.0634x + 1.566	0.2615	y = 2.2493x - 0.424	0.2996	Pseudo-second order
Naphthol using unmodified rice husks	y = 0.0649x + 1.6027	0.2613	y = 3.5387x - 0.3495	0.2975	Pseudo-second order
anthracene using modified rice husks	y = 0.0537x + 1.6488	0.241	y = 2.525x - 0.3716	0.2703	Pseudo-second order
anthracene using unmodified rice husks	y = 0.0561x + 1.683	0.2503	y = 2.594x + 0.0152	0.2493	Pseudo-first order

Based on Table 2's results, it is clear that K1's coefficient correlation (R^2) values were greater than K2's, which would be represented as K1> K2.

Therefore K1 provides the best R^2 values, the experimental findings showed that optimum variation were achieved with this value. Thus, it can be concluded that the pseudo-first order kinetic model (K1), as opposed to the pseudo-second order (K2), suited the experimental data the best. This was consistent with research conducted by Barrera (2020), Nayak *et al.* (2020), and Kaman *et al.* (2016).

IV. Conclusion

Rice husks was effectively functionalized with ethylamine as the structure of cellulose in rice husks was anchored with triethylamine. This increased the sorption capacity towards phenolate ions. The modification procedure was done by first chlorinating and then aminating rice husks to form a quaternary amine cellulose. The FT-IR analysis confirmed the presence of the functional groups which performed as the binding sites for adsorption of phenols. The Fourier Transform Infrared (FT-IR) confirmed modification at 3424.67cm-1. The NMR analysis indicated that the adsorbent has a structure like that of a cellulose. The presence of carbons atoms attached with chlorine atom and from ethylene diamine amine were confirmed by 13C NMR analysis. That confirmed the presence of each respective substitution of the desired atom or functional group on within the structure of the cellulose material was successful. An amine groups were successfully anchored in rice husks wastes. Analysis using scanning electron microscope showed that the modified rice husks was more porous than the unmodified rice husks. The modified rice husks was affected by the pH of water, phenol concentration, contact time and adsorbent dosage. It was observed that the pH of optimum adsorption was 5.5 for all the phenols and the uptake was more than 90% within the first 2 min of contact time. The adsorption suggested to Langmuir model of monolayer adsorption with correlation coefficient (R^2) of 0.9895 for Naphthol. Whereas the kinetics confirmed to be chemisorption process. Removal of Naphthol with modified rice husks gave the best adsorption capacity of 0.6125 mg/g. Thus modified rice husks can be used as an effective adsorbent material for elimination of phenolic compounds from unsafe drinking water

References

[1] Abbaszadegan, A., Ghahramani, Y., Gholami, A., Hemmateenejad, B., Dorostkar, S., Nabavizadeh, M. And Sharghi, H. (2015). The Effect Of Charge At The Surface Of Silver Nanoparticles On Antimicrobial Activity Against Gram-Positive And Gram-Negative Bacteria: A Preliminary Study. Journal Of Nanomaterials, 16: 1-8

[2] Arefieva, O. D., Pirogovskaya, P. D., Panasenko, A. Y., Kovekhova, A. V., & Zemnukhova, L. A. (2021). The Acid-Base Properties Of Amorphous Silica From Straw And Rice Husk. Chemistry Of Plant Raw Material, (1), 327-335.

Https://Doi.Org/10.14258/Jcprm.2021017521
[3] Ali, I., Mohd. A. And Tabrez, A. (2012). Low Cost Adsorbents For The Removal Of Organic Pollutants From Wastewater. Journal Of Environmental Management; 113: 170-183.
[4] Ali, I. And Aboul, H. (2004). Chiral. Pollutants: Distribution, Toxicity And Analysis By Chromatography And Capillary Electrophoresis. John Wiley & Sons, Chichester,Amin, N.A.S., Akhtar, J., Rai, H.K., (2010). Screening Of Combined Zeolite-Ozone System For Phenol And Cod Removal. Chem. Eng. J. 158, 520–527r For Industrial Treatment Of Wastewater. Energy Procedia 18, 395–403.
[5] Barlow, R.B., (1976). The Effects Of Ph On The Activity Of Coryneine And Related Phenolic Quaternary Ammonium Salts On The Frog Rectus Preparation. Br. J. Pharmacol. 57 (4).
[6] Brundle, R., Evans, J. And Wilson, S. (1992). Encyclopedia Of Materials Characterization: Surfaces, Interfaces, Thin Films.
[7] Burkhard, L. And Lukazewycz, M. (2008). Toxicity Equivalency Values For Polychlorinated Biphenyl Mixtures. Environmental Toxicology And Chemistry, 27: 529–534
[8] Burghoff, B., De Haan, A.B., (2009). Liquid–Liquid Equilibrium Study Of Phenol Extraction With Cyanex 923. Sep. Sci. Technol. 44, 1753– 1771.
[9] Cagnoli, B. (2016). The Channel Width Effect Has Never Been Studiedbefore. Https://Doi.Org/10.5194/Se-2016-79-Ac3
[10] Chakroff, M., & Corps, P. (2015). Freshwater Fish Pond Culture And Management. Scientific Publishers - Ubp
[11] Campanale, C., Massarelli, C., Savino, I., Locaputo V.And Vito Felice V. U. (2020)
[12] A Detailed Review Study On Potential Effects Of Microplastics And Additives Of Concern On Human Health, International Journal Of Environmental Research And Public Health,17, 1212; Doi:10.3390/Ijerph17041212
[13] Cao, Z., He, Y. H., Sun, L. X., & Cao, X. Q. (2011). Application Of Chemical Engineering. Trans Tech Publications.
[14] Cheng, Z. L., & Han, G. (2020). Design Of Other Pressure Retarded Osmosis Hybrid Processes (Pressure Retarded Osmosis–Membrane Distillation And Pressure Retarded Osmosis–Forward Osmosis). Membrane Technology For Osmotic Power Generation By Pressure Retarded Osmosis, 285-323.
[15] Choi, K., Kima, S. And Kim, S. (2008). Removal Of Antibiotics By Coagulation And Granular Activated Carbon Filtration. Journal Of Hazardous Materials, 151(1): 38-43
[16] Chedeville, O., Debacq, M., Porte, C., (2009). Removal Of Phenolic Compounds Present In Olive Mill Wastewaters By Ozonation. Desalination 249, 865–869. 348–356
[17] Crisponi, G., Casu, M., Nurchi, M., Cesare-Marincola, F., Pivetta, T. And Silvagni, R. (2002). Substituent Effects On Ionisation And 13c Nmr Properties Of Some Monosubstituted Phenols; A Potentiometric, Spectrophotometric And 13c Nmr Study. Talanta, 56: 441-449.
[18] Cui, H., Abu-Siada, A., Li, S., And Islam, S. (2017). Correlation Between Dissolved Gases And Oil Spectral Response. In 2017 1st International Conference On Electrical Materials And Power Equipment. Ieee. Pp. 28-32
[19] Damia, B. (2005). Emerging Organic Pollutants In Waste Waters And Sludge. Springer, Berlin,
[20] De, D., Santosha, S., Aniya, V., Sreeramoju, A., And Satyavathi, B. (2018). Assessing The Applicability Of An Agro-Industrial Waste To Engineered Bio-Char As A Dynamic Adsorbent For Fluoride Sorption. Journal Of Environmental Chemical Engineering, 6: 2998-3009
[21] Duan W, Meng F, Lin, Y, Wang G (2017) Toxicological Effects Of Phenol On Four Marine Microalgae, Environmental Toxicology And Pharmacology 52 170–176, Dx.Doi.Org/10.1016/J.Etap.2017.04.006
[22] Faria, A., Maldaner, L., Santana, C., Jardim, I. And Collins, C. (2007). Poly (Methyltetradecylsiloxane) Immobilized Onto Silica For Extraction Of Multiclass Pesticides From Surface Waters. Analytica Chimica. Acta, (582 (1): 34-40.
[23] Fu, J., Chen, Z., Wang, M., Liu, S., Zhang, J., Zhang, J. And Xu, Q. (2015). Adsorption Of Methylene Blue By A High-Efficiency Adsorbent (Polype-Vloamine Microspheres): Kinetics, Isotherm, Thermodynamics And Mechanism Analysis. Chemical Engineering Journal, 259: 53-61.
[24] Georgopoulos, S., Tarantili, P., Avagerinos, E., Reopoulos, A. And Koukios, E. (2005). Thermoplastic Polymers Reinforced With Fibrous Agricultural Residues. Journal Of Polymeric Degredation Stability, 90(2): 303-312.
[25] Gillen, M. (2001). 147. Lessons Learned From The Epa/Osha Chemical Advisory: “Skin Exposure To Molten 2,4-Dichlorophenol (2,4-Dcp) Can Cause Rapid Death”. Aihce 2001. Https://Doi.Org/10.3320/1.2765661
[26] Giri, A., Osako, K., Okamoto, A., Okazaki, E., & Ohshima, T. (2012). Effects Of Koji Fermented Phenolic Compounds On The Oxidative Stability Of Fish Miso. Journal Of Food Science, 77(2), C228-C235. Doi:10.1111/J.1750-3841.2011.02540.Xgrushka, E., & Grinberg, N. (2012). Advances In Chromatography. Crc Press.
[27] Han, R., Zhang, L., Song, C., Zhng, M. Zhu, M. And Zhang, L. (2010). Characterization Of Modified Wheat Straw, Kinetic And Equilibrium Study About Copper Ion And Methylene Blue Adsorption In Batch Mode. Carbohydrate Polymers, 79: 1140-1149.
[28] Harrad, S. (2001). Persistent Organic Pollutants Environmental Behaivour And Pathways For Human Exposure. Kluwer Academic Publishers, Norwell.
[29] Henini, G., Laidani, Y., Souahi, F., Hanini, S., (2012). Study Of Static Adsorption System Phenol/Luffa Cylindrical Fibe
[30] Hentabli, M., Belhadj, A. E., & Dahmoune, F. (2021). Dragonfly Support Vector Machine Modelling Of The Adsorption Phenomenon Of Certain Phenols By Activated Carbon Fibres. Kemija U Industriji, (9-10). Https://Doi.Org/10.15255/Kui.2020.073
[31] Hubicki, Z., & Koodynsk, D. (2012). Selective Removal Of Heavy Metal Ions From Waters And Waste Waters Using Ion Exchange Methods. Ion Exchange Technologies. Doi: 10.5772/51040
[32] Hussain, C. M., & Kadeppagari, R. K. (2022). Undefined. John Wiley & Sons.
[33] Igberase, E., Osifo, P. O., Seodigeng, T., & Emeji, I. (2021). Enhanced Chitosan Material For Water Treatment: Applications Of Multi-Functional Chitosan Derivative. Springer Nature.
[34] James, T. (2012). Nuclear Magnetic Resonance In Biochemistry. Elsevier.
[35] Jin, L And Preston, A.F (1991) The Interaction Of Wood Preservative With Lignocellulosic Substrates, Holforschung, 45 455-459.
[36] Kaman Singh, B. Chandra And M. Gautam (2016). Development Of Inexpensive Adsorbent From Agro-Waste For Phenol Adsorption. Journal Of Scientific & Industrial Research, Researchgate, 75, 444-451.
[37] Kamble, S., Deshpande, G., Barve, P., Rayalu, S., Labhsetwar, N., Malyshew, A. And Kulkarni, B. (2010). Adsorption Of Fluoride From Aqueous Solution By Alumina Of Alkoxide Nature: Batch And Continuous Operation. Desalination, 264: 15-23
[38] Kogan, M., Metz, A., & Ortega, R. (2003). Adsorption Of Glyphosate In Chilean Soils And Its Relationship With Unoccupied Phosphate Binding Sites. Pesquisa Agropecuária Brasileira, 38(4), 513-519. Https://Doi.Org/10.1590/S0100-204x2003000400010
[39] Lateef, A., Gueguim-Kana, E. B., Dasgupta, N., & Ranjan, S. (2021). Microbial Nanobiotechnology: Principles And Applications. Springer Nature.
[40] Lawrance, S., Bajpai, J. And Bajpai, A. (2011). Designing Fixed Bed Column And Batch Studies Of Chitosan Nanoparticles For Defluoridation Of Drinking Water. Journal Of Dispersion Science And Technology, 32: 1256-1265.

[41] Liu, Q.-S., Zheng, T., Wang, P., Jiang, J.-P., Li, N., (2010). Adsorption Isotherm, Kineticand Mechanism Studies Of Some Substituted Phenols On Activated Carbon Fibers. Chem. Eng. J. 157 (2–3).

[42] Martos, N.R., Sánchez, A.G., Díaz, A.M., (2005). Comparative Study Of The Retention Of Nine Phenolic Compounds On Anionic Exchanger Resins. Chem. Pap. 59 (3).

[43] Moeder, M. (2006). Phenols Analysis In Environmental Samples. Encyclopedia Of Analytical Chemistry. Doi:10.1002/9780470027318.A0854

[44] Mohammed, S., & Fasnabi, P. (2016). Removal Of Dicofol From Waste-Water Using Advanced Oxidation Process. Procedia Technology, 24, 645-653. Doi:10.1016/J.Protcy.2016.05.160

[45] Moran, J., Alvarez, V., Cyras, V. And Vázquez, A. (2008). Extraction Of Cellulose And Preparation Of Nanocellulose From Sisal Fibers. Cellulose, 15:149–159.

[46] Mota, F L., Queimada, A ,J., Pinho, S P.; Macedo, E A. (2008). Aqueous Solubility Of Some Natural Phenolic Compounds. Industrial & Engineering Chemistry Research, 47(15), 5182–5189. Doi:10.1021/Ie071452o

[47] Muthukumaravel, K., Prithiviraj, N., Ramesh, M., Sekar, V. And Sheik, M. S. (2013). Light And Scanning Electron Microscopic Evaluation And Effects Of Cadmium On The Gills Of The Fresh Water Fish, Labeo Rohita. International Journal Of Pharmaceutical And Biological Archives, 4 (5): 999 - 1006.

[48] Muthukumaravel, K. And Rajaraman, P. (2013). A Study Of The Toxicity Of Chromium On The Histology Of Gill And Liver Of Freshwater Fish Labeo Rohita. Journal Of Pure And Applied Zoology, 1 (2): 122 – 126

[49] Mwangi Iw, Ngila Jc. Okonkwo Jo. (2012): A Comparative Study Of Modified And Unmodified Maize Tassels For Removal Of Selected Trace Metals In Contaminated Water, Toxicological & Environmental Chemistry, 94:1, 20-39

[50] Nurzyńska-Wierdak R. (2023) Phenolic Compounds From New Natural Sources-Plant Genotype And Ontogenetic Variation.Molecules.;28 (4):1731. Doi: 10.3390/Molecules28041731.

[51] Nie, B., Liu, X., Yang, L., Meng, J. And Li, X. (2015). Pore Structure Characterization Of Different Rank Coals Using Gas Adsorption And Scanning Electron Microscopy. Fuel, 158: 908-917

[52] Niide Teppei , Hikaru Tatsuya Shirakioshima (2010). Quaternary Ammonium Bacterial Cellulose For Adsorption Of Proteinssolvent Extraction Research And Development.

[53] Okoro, I. And Okoro, S. (2011). Agricultural By Products As Green Chemistry Absorbents For The Removal And Recovery Of Metal Ions From Waste-Water Environments. Continental Journal Of Water, Air And Soil Pollution, 2(1): 15–22.

[54] Okoro, I., Oriaku, C. And Ejike, E. (2007). Lead Characterization Of Street Dust In Some Cities In Southeastern Nigeria. Research Journal Of Applied Sciences, 2: 39 -43.

[55] Oszmiański J, Kolniak-Ostek J1,* And Biernat A (2015) The Content Of Phenolic Compounds In Leaf Tissues Of Aesculus Glabra And Aesculus Parviflora Walt. Molecules, 20, 2176-2189.

[56] Paßlack, N., Mainzer, B., Lahrssen-Wiederholt, M., Schafft, H., Palavinskas, R., Breithaupt, A., Neumann, K., & Zentek, J. (2014). Concentrations Of Strontium, Barium, Cadmium, Copper, Zinc, Manganese, Chromium, Antimony, Selenium And Lead In The Equine Liver And Kidneys. Springerplus, 3(1). Https://Doi.Org/10.1186/2193-1801-3-343

[57] Park, S., Johnson, D., Ishizawa, C., Parilla, P. And Davis, M. (2009). Measuring The Crystallinity Index Of Cellulose By Solid State 13 C Nuclear Magnetic Resonance. Cellulose, 16: 641-647.

[58] Pasquini, L. (2020). Advances In Nanoparticles: Synthesis, Characterization, Theoretical Modelling, And Applications. Mdpi

[59] Pramesti, K. A., Kusumadewi, R. A., & Hadisoebroto, R. (2021). Undefined. Iop Conference Series: Earth And Environmental Science, 737(1), 012014. Https://Doi.Org/10.1088/1755-1315/737/1/012014

[60] Parisi, S. (2019). Analysis Of Major Phenolic Compounds In Foods And Their Health Effects. Journal Of Aoac International, 102(5), 1354-1355. Doi:10.1093/Jaoac/102.5.1354

[61] Patnaik, P. (2017). Phenols. Handbook Of Environmental Analysis,277-280. Doi:10.1201/9781315151946-49

[62] Patil, V., & Woo, E. (2016). Undefined. Https://Doi.Org/10.2210/Pdb5frw/Pdb

[63] Patisaul, H. B., & Belcher, S. M. (2017). Landmark Endocrine-Disrupting Compounds Of The Past And Present. Oxford Scholarship Online. Https://Doi.Org/10.1093/Acprof:Oso/9780199935734.003.0003

[64] Pramesti, K. A., Kusumadewi, R. A., & Hadisoebroto, R. (2021). Undefined. Iop Conference Series: Earth And Environmental Science, 737(1), 012014. Https://Doi.Org/10.1088/1755-1315/737/1/012014

[65] Qiu, N. Li,H. Xu,E. Qin J., And Zheng,L. (2012)“Temperature And Time Effects On Free Radical Concentration In Organic Matter: Evidence From Laboratory Pyrolysis Experimental And Geological Samples,” Energy Exploration And Exploitation, Vol. 30, No. 2, Pp. 311–330,

[66] Radia, A (2019). [Studies In Natural Products Chemistry] Bioactive Natural Products Volume 63 || Phytochemistry And Biological Activities Of Algerian Centaurea And Related Genera. , (), 357–414. Doi:10.1016/B978-0-12-817901-7.00012-5

[67] Ruiz, B., Cabrita, I., Mestre, S., Parra, J., Pires, J., Carvalho, A. And Ania, C. (2010). Surface Heterogeneity Effects Of Activated Carbons On The Kinetics Of Paracetamol Removal From Aqueous Solution. Applied Surface Science, 256: 5171-5175.

[68] Soto-Hernández, Marcos; Palma-Tenango, Mariana; Garcia-Mateos, Maria Del Rosario (2017). Phenolic Compounds - Natural Sources, Importance And Applications || Chemical Structure Of Phenols And Its Consequence For Sorption Processes. , 10.5772/67213(Chapter 1), –. Doi:10.5772/66537

[69] Saidi, F., Taulelle, F. And Martineau, C. (2016). Quantitative 13c Solid-State Nmr Spectra By Multiple-Contact Cross-Polarization For Drug Delivery: From Active Principles To Excipients And Drug Carriers. Journal Of Pharmaceutical Sciences, 105: 2397-2401

[70] Sam, S. R. (2017). Nano-Physics: Zns Nanoparticles. Csmfl Publications.

[71] Singh, B. (2015) Comparative Study On Removal Of Fluoride From Groundwater By Natural And Modified Bagasse Carbon Of Sugarcane. International Research Journal Of Pure And Applied Chemistry, 8: 147-156.

[72] Singh, S. K., & Dhepe, P. L. (2022). Undefined. Waste And Biomass Valorization, 13(6), 2963-2977.

[73] Sharafian, A., & Bahrami, M. (2013). Undefined. International Journal Of Heat And Mass Transfer, 59, 262-271. Https://Doi.Org/10.1016/J.Ijheatmasstransfer.2012.12.019

[74] Sorlini, S., Biasibetti, M., Gialdini, F., & Collivignarelli, M. C. (2017). Removal Of Chlorite From Drinking Water: Laboratory And Pilot Scale Studies To Predict Activated Carbon Performance At Full Scale.

[75] Soto-Hernández, M., Tenango, M. P., & García-Mateos, R. (2017). Phenolic Compounds: Natural Sources, Importance And Applications. Bod – Books On Demand.

[76] Srivastava, V.C., Mall, I.D., Mishra, I.M., (2007). Adsorption Thermodynamics And Isosteric Heat Of Adsorption Of Toxic Metal Ions Onto Bagasse Fly Ash (Bfa) And Rice Husk Ash (Rha). Chem. Eng. J. 132, 267–278.

[77] Sud, D., Mahajan G. And Kaur, M. (2008). Agricultural Waste Material As Potential Adsorbent For Sequestering Heavy Metal Ions From Aqueous Solutions. A Review. Bioresource Technology, 99: 6017-6027.

[78] Tian, L., Jiang, H., Chen, P., Wang, Q., Niu, P., Shi, Y. And Luo, X. (2018). A Novel Go/Pnipam Hybrid With Two Functional Domains Can Simultaneously Effectively Adsorb And Recover Valuable Organic And Inorganic Resources. Chemical Engineering Journal, 343: 607-618.

[79] Wang, H., Liu, W., Yao, W., Zhang, K., Zhong, J., & Chen, R. (2013). Quaternary Ammonium Salts Intercalated A-Zrp Compounds For Adsorption Of Phenolic Compounds. Applied Surface Science, 268, 179-187. Doi:10.1016/J.Apsusc.2012.12.054.

[80] Wang, L. Y., Wang, F. Y., & Wang, B. B. (2011). A Novel Method For Preparation Of Antimicrobial Cellulose Textile By Surface Carbamatization And N-Chlorination. Advanced Materials Research, 399-401, 1088-1092.

[81] Yakout, A. A., Shaker, M. A., Elwakeel, K. Z., And Alshitari, W. (2018). Lauryl Sulfate@ Magnetic Graphene Oxide Nanosorbent For Fast Methylene Blue Recovery From Aqueous Solutions. Journal Of Dispersion Science And Technology, 3: 1-9.Yu, P., Chang, Z., Ma, Y., Wang, S., Cao, H., Hua, C., Liu, H., (2009). Sep. Purif. Technol. 70, 199–206.

[82] Zagoskina, N. V., Nikolaeva, T. N., Lapshin, P. V., Zavarzin, A. A., & Zavarzina, A. G. (2013). Water-Soluble Phenolic Compounds In Lichens. Microbiology, 82(4), 445-452. Doi:10.1134/S0026261713030132

[83] Zaini, N., & Kamarudin, K. (2018). Effect Of Concentration On Amine-Modified Kenaf As A Sorbent For Carbon Dioxide Adsorption In A Pressure Swing Adsorption System. Chemengineering, 2(2), 23.

[84] Zhou, W., Apkarian, R., Wang, Z. L. And Joy, D. (2006). Fundamentals Of Scanning Electron Microscopy (Sem). Scanning Microscopy For Nanotechnology. Springer, New York, Ny. Pp. 1-40.

[85] 张, 张., & Li, H. (2023). Phenol Removal By Activated Blood Carbon Treatment On The Sorption Capacity: A Kinetic, Isotherm And Thermodynamic Study. Https://Doi.Org/10.2139/Ssrn.4419130