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GRAFTED SILICA WITH APTES/PARACETAMOL USED IN THE REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTIONS AT THREE DIFFERENT TEMPERATURE

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ABSTRACT
Modified silica/aptes/paracetamol was synthesized from rice husk ash as a source of silica and successfully functionalized with APTES and paracetamol by grafting method was characterized using infrared Spectroscopy (FTIR), Scanning Electron Spectroscopy (SEM), X-ray diffraction analysis (XRD) and Energy-dispersive x-ray spectroscopy (EDX). The ability of the modified silica to adsorb methylene blue from aqueous solution was evaluated using modified silica and the effect of three temperatures (298, 303, and 313 (K) was carried out by adsorption process. The study findings clearly showed that synthesized silica/aptes/paracetamol was very efficient in removing methylene blue from aqueous solution and also, various adsorption studies were carried out and the isotherm models were also investigated. Based on the adsorption parameters obtained different models were used but Langmuir model was the best process found to be for adsorption studies. The R^2 regression coefficient was 0.9989.
Keywords: Characterization; adsorption; efficiency; methylene blue; modified silica/aptes/ paracetamol.

INTRODUCTION

Silica is grafted because of it has the ability to increase surface area which enhances the removal of materials from different media. The scale of nanomaterials, according to the US National Nanotechnology Initiative, ranges from 1 to 100 nm Ali *et al*., (2020). According to Anad *et al*., (2019) and Mageed *et al*., (2019) dyes are considered because of their carcigenoic properties and also pollutants such as heavy metals, phenols, medications, and so on are extremely hazardous to human health and aquatic life. In the age of current technology, industrial dyes are used everywhere. Dyes are water-soluble pigments used to color papers, skins, hair, meals, cosmetics, and clothing. The removal of dyes from industrial wastewater is critical and has received a lot of attention in recent years due to their toxicity Amel *et al*., (2020) and the demand for clean water, which is predicted to expand dramatically as industrialisation increases.The disposal of industrial effluents endangers the environment and is becoming a major worry for human society's long-term growth. Waste water reclamation and recycling are critical aims for protecting the global ecology and improving environmental quality Nadhir *et al*., (2016).

Silica particles are widely employed as fillers, catalyst carriers, and biological and pharmaceutical materials in a variety of sectors Bing *et al*., (2012).To improve application performance, their surfaces are generally changed by functional chemical groups .Because of its amino group, 3-aminopropyltriethoxysilane (APTES) is a regularly utilized coupling agent and paracetamol was used as drug delivery. Kim *et al*., (2010). Microporous inorganic adsorbents (e.g., zeolites) and silica with unique surface and pore properties as well as high surface areas have recently been widely explored as carbon adsorbent alternatives for liquid adsorption of dissolved contaminants in water Karim *et al*., (2012).

Surface functionalization by organic groups on mesostructured materials has been used for purposes of utilizing post-grafting Wang et al., (2009). A simple approach is hereby presented where silica is grafted with 3-aminopropyl triethoxysilane serving as pore expander, thereby producing a mesostructured material with a large specific surface area. Paracetamol serve to enhance the adsorptive capacity of silica/aptes/paracetamol compound. Analytical techniques such as X-ray diffraction, fourier transform infrared spectroscopy, energy dispersive x-ray diffraction (EDX) and scanning electron microscopy (SEM) were used to analyze the modified silica/aptes/paracetamol and used in the adsorption of methylene blue (MB) from pure solutions. Various adsorption studies were carriedout and the isotherm models were also investigated.

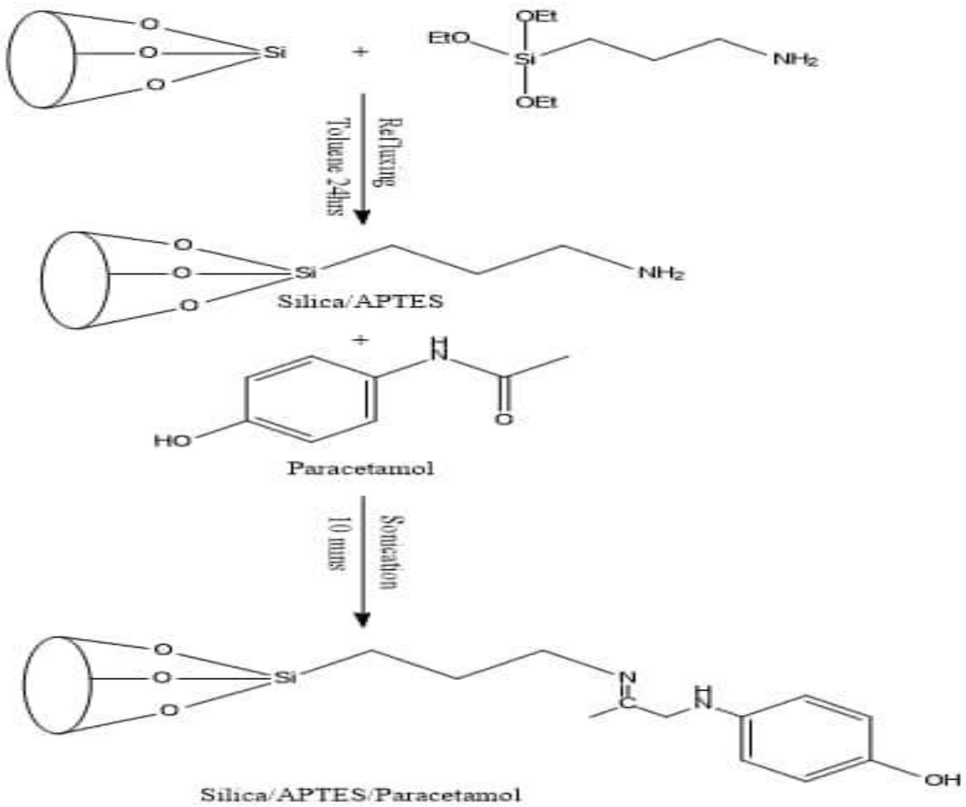
As a result, the goal of this work was to get silica from rice husk ash (RHA) that had been treated with APTES and paracetamol and was specifically engineered to adsorb various contaminants such as dyes from wastewater.

MATERIAL AND METHODS

All chemicals were used in this work of analytical grade. APTES, Paracetamol and other chemicals were purchased from Sigma aldrich.

Preparation of Modified Silica/APTES/paracetamol

About 5g of silica dispersed in a solvent (toluene) 20 ml, 3 ml of APTES was added into the solution 100 ml of ethanol. The dispersion was stirred for 24 hours at under reflux at 110^0 C. The grafted silica was separated by centrifuging for 15 mins at 15,000rpm 3 times and washed with ethanol and water 2 times (to remove excess APTES) Mariana *et al.*, (2020).The purified SiO_2 / APTES was kept dispersed in ethanol and finally was dried for 24 hours at 60^0 C to evaporate volatile solvents. 5g of silica/APTES and 1.5g of pure paracetamol was mixed, 15 ml of ethanol was added to the mixture. The mixture was ultrasonicated for 10 mins. Dried at room temperature for 48 hours Marieh *et al.*, (2021).



Schematic representation of silica/aptes/paracetamol

Grafted behavior silica/aptes/paracetamol adsorption

For methylene blue (MB), the adsorption performance of synthesized silica/aptes/paracetamol was examined. The methylene blue dye stock solution was made by dissolving 1 g of the methylene blue dye in an appropriate volume of distilled water and then diluting to 1000 mL to get a 1000 ppm solution. 100 mL of different concentrations of MB solutions in distilled water were produced from this stock solution. To conduct an adsorption experiment, silica/aptes/paracetamol with different concentrations were produced. Then, in 100 mL volumetric flasks, 10 mL of each concentration were taken and 0.05 g of the silica/aptes/paracetamol was added. The flask contents were shaken for 1 hour at 25°C, filtered using vacuum pump filtration. The adsorption of these dyes was tracked by capturing UV-Vis spectral changes over time Peng *et al.*, (2017). To calculate the equilibrium Ci (mg/L) concentration of each solution, the calibration curve was created, and the amount of adsorbent substance Qe (mg/g) in all situations was calculated using the formula below as described by Asiagwu (2013),

$$Qe = (C_i - C_f)\frac{V}{M}$$

Where:

Qe= Adsorption efficiency/binding capacity.

C_i = Initial dye concentration in solution (mg/L) at equilibrium.

C_f = final dye concentration in solution (mg/L)

V = volume of dye solution used (L)

M = mass of adsorbent used (g)

RESULTS AND DISCUSSION

FTIR analysis. Figure 2 illustrates the FT infrared spectra of modified silica recorded in the region 4000–400 cm^{-1}. For both samples, the absorption peaks at 1000 cm^{-1}, 790 cm^{-1}, and 800 cm^{-1} were assigned to asymmetric, symmetrical stretching and bending vibration of Si–O–Si bond, respectively. Te spectral band at 1600 cm^{-1} in samples is due to the –OH deformation band of water molecules remained in the matrix. For the silica/NH_2 sample, the band at 1500 cm^{-1} in the spectrum indicated the existence of the N–H bending vibration of the –NH_2 groups. Two bands at 2880 cm–1 and 2582 cm–1 are corresponded to the CH of the –CH_2 groups of propyl chain, indicating the successful formation of amine groups after modifcation.

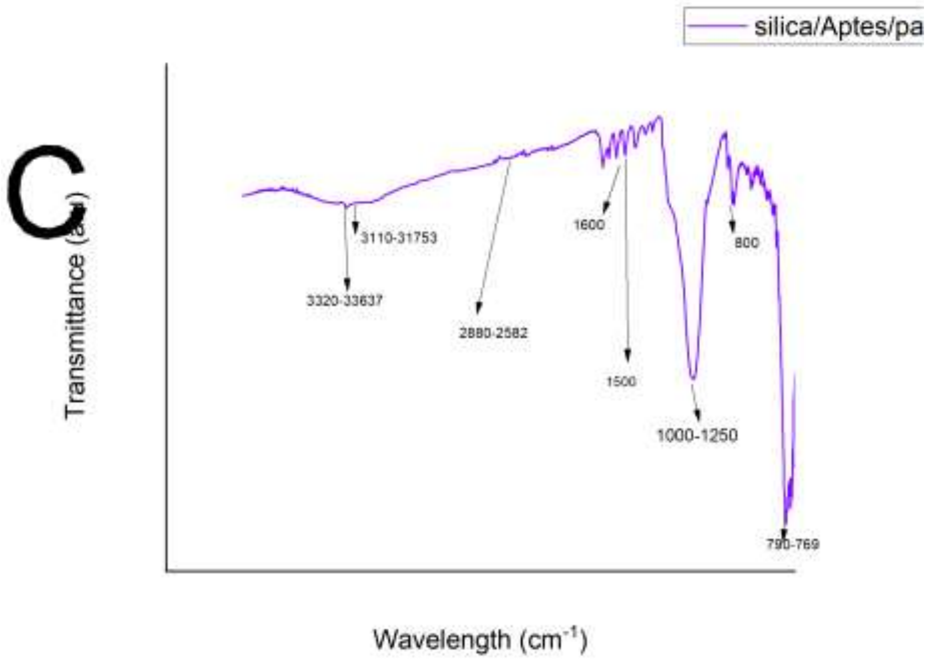


Figure 1: FTIR spectrum of silica/aptes/paracetamol

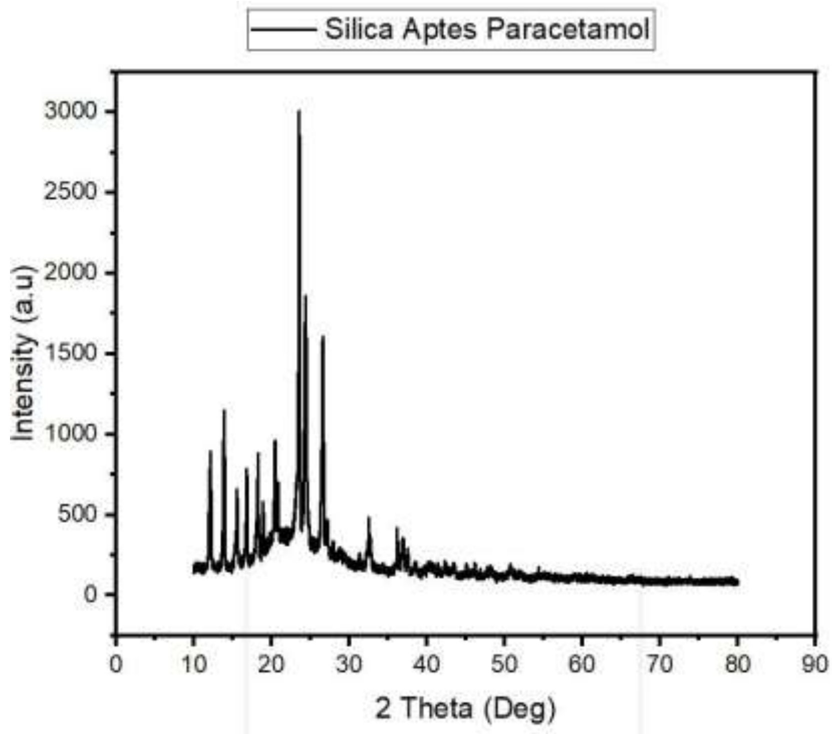


Figure 2: XRD patterns of silica/aptes/paracetamol

The silica/aptes/paracetamol XRD patterns (Fig. 2) were distinguished by a large peak at about 2θ = 25.2^0, revealing that the modified silica matrix which is connected to the intra-chain segment distance.The presence of rigid aromatic rings in the XRD pattern was caused by the aromatic group, which leads to more rigid structures and is more prone to crystallization than completely aliphatic groups.The modified silica has small broad peaks at 10.13°, 12.25°, 16.78°, 20.35°, 24.14o, 25.00^o, 31.00^{o,} and 38.60°.The observation of sets of matching lattice planes may be properly indexed to the silica/APTES/paracetamol facts (111), (200), (220), and (311). Furthermore, it is obvious that as the concentration of APTES in a silica-functionalized composite increases,The intensity and narrowness of the diffraction peaks increase, meaning that the average particle size is likewise rising.

Spectrum 1				
Element	**Line Type**	**Weight %**	**Weight % Sigma**	**Atomic %**
Si	K series	21.97	0.81	12.38
O	K series	44.31	1.63	43.81
C	K series	32.89	2.11	43.32
Cl	K series	0.35	0.09	0.16
Na	K series	0.48	0.16	0.33
Total		100.00		100.00

Figure 3: EDX spectra of silica/aptes/paracetamol

Figure 3, shows the modified silica/aptes/paracetamol EDX analysis confirms the presence of constituents element and heterogeneous distribution of APTES/paracetamol on the silica surface.

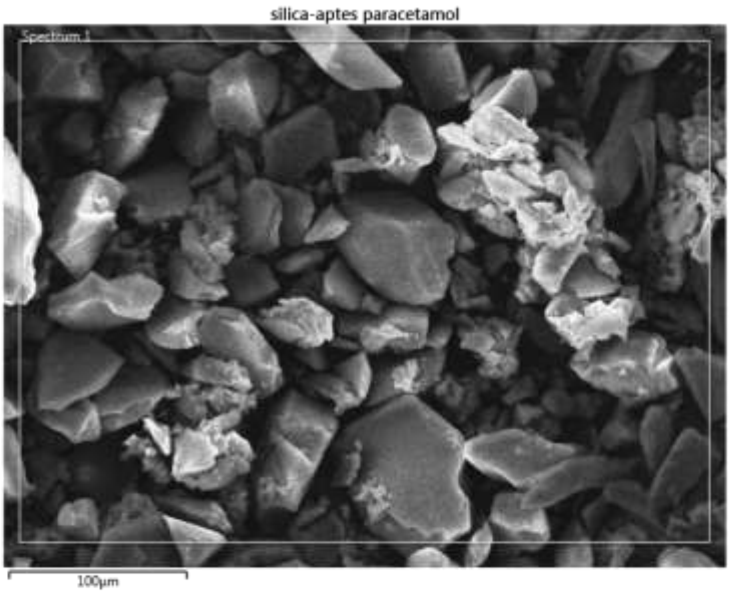


Figure 4: Morphology of silica/aptes/paracetamol

SEM was used to examine the surface morphology of functionalized silica. The micrograph revealed that the modified silica is evenly distributed on the surface, with primarily spherical shapes at the nanoscale. However, it was discovered that the size of the nanocomposites increased from 1-25 to 1-100um. The strong attraction of paracetamol to silica/APTES could be attributed to electrostatic interaction between the materials and electroactive species.

Adsorption of methylene blueusing three different temperatures

Table 1 shows the effect of temperature on adsorption of methylene blue pigment on the surface of grafted silica has been studied within the thermal range (298, 303 and 313 K). The experimental results showed that the adsorption of the methylene blue pigment on the surface of these grafted silica which prepared, decreases with increasing temperature, meaning that the process is endothermic process. This indicates the presence of a desorption process, meaning the separation of the adsorbed particles on the adsorbent surface, and its return to the solution, thereby reducing speed diffusion of molecules with rising the temperature as shown in Figure (5a, b, c).

TABLE 1. Effect of temperature on adsorption of methylene blue dye

Conc	Temp	Grafted silica/aptes/paracetamol	
		Ce	Qe
5ppm	298K	0.371	248.0
	303K	0.388	235.2
	313K	0.724	145.0
10ppm	298K	1.378	400.2
	303K	1.538	353.6
	313K	1.899	197.2
15ppm	298K	2.707	672.2
	303K	2.847	564.0
	313K	3.956	323.6

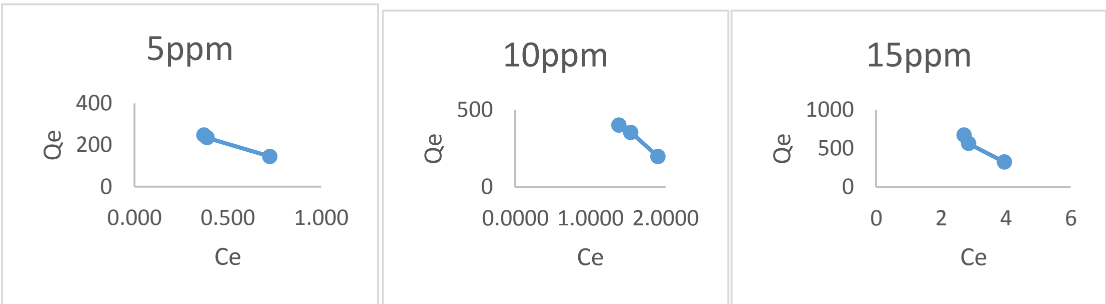


Figure 5; Effect of temperature on adsorption of grafted silica at (5, 10 and 15ppm) at 298K (a); 303K (b); 313K (c)

Effect of concentration of dye on adsorption: Adsorption isotherms are usually determined under equilibrium conditions. A series of different initial dye concentration experiments for MB dye have been carried out (5–60 mg/L) and at maximum temperature. Table 2 shows the initial concentration for MB dye to reach equilibrium at 1 h. However, for MB dye with higher initial concentrations (60 mg/L) at different temperatures. As can be seen from table 1, the amount of the adsorbed dye onto modified silica increases with time and, at some point in time, reaches a constant value beyond which no more is removed from solution. At this point, the amount of the dye desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of the dye being adsorbed onto the modified silica. The time required to attain this state of equilibrium is termed the equilibrium time, and the amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions at different temperatures.

Table 2 shows the initial concentration of methylene blue dye

Conc (mg/L)	Conc at Equib (Ce)	Binding Capa (Qe)	Ce/Qe
5	4.6	5.5	0.8
10	6.6	7.5	0.9
15	11.5	12.6	0.9
20	14.5	13.7	1.1
25	16.4	16.5	1.0
30	18.7	17.7	1.1
35	26.4	16.2	1.6
40	30.6	15.5	2.0
45	36.4	16.0	2.3
50	38.5	16.9	2.3
55	40.5	16.9	2.4
60	44.1	16.7	2.6

Langmuir Isotherm Evaluation Process

The maximal adsorption capacity corresponding to complete monolayer coverage on the biomass surface was estimated using the Langmuir isotherm model. The linear flow between the specific adsorption (Ce/Qe) against the equilibrium concentration (Ce) are represented in Table 2 and the linear isotherm . constants; The R^2 regression coefficient was 0.9989, this suggests that the Langmuir Isotherm (R^2) obtained provides a good model of the adsorption process, by implication it is a monolayer surface adsorption process with favourable process since KL (0.601) < 1.

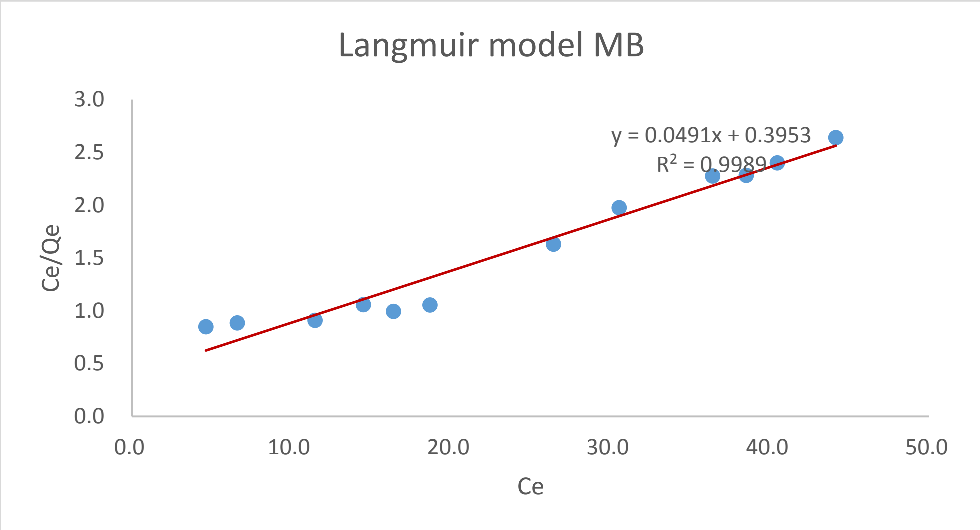


Fig 6: langmuir isotherm for adsorption of methylene blue dye on the surface of grafted silica/aptes/paracetamol

CONCLUSION

A novel and successful method for modifying the surface of silica particles with APTES/paracetamol was devised, which was possible to produce a high grafting density on the silica surface. The ability of modified silica to remove methylene blue dye from aqueous solution has been studied. It was observed that increase in the content of methylene blue dye adsorbed with three different temperatures (298K, 303K, and 313K) increases with decreasing temperatures. The ability of the adsorbent in the removal of methylene blue dye was well described by the Langmuir isotherm models because different parameters were used. The modified silica is thus a good adsorbent for the removal of methylene blue dye from aqueous solution. This can be enlarged and adopted in industrial scale; hence the optimum conditions to operate this process have been determined.

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