

Adsorption of Copper by using Microwave Incinerated Rice Husk Ash (MIRHA)

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Abstract—Many non-conventional adsorbent have been studied as economic alternative to commercial activated carbon and mostly agricultural waste have been introduced such as rubber leaf powder and hazelnut shell. Microwave Incinerated Rice Husk Ash (MIRHA), produced from the rice husk is one of the low-cost materials that were used as adsorbent of heavy metal. The aim of this research was to study the feasibility of using MIRHA500 and MIRHA800 as adsorbent for the removal of Cu(II) metal ions from aqueous solutions by the batch studies. The adsorption of Cu(II) into MIRHA500 and MIRH800 favors Freundlich isotherm and imply pseudo – kinetic second order which applied chemisorptions

Keywords—Copper (II) aqueous solution, batch study, MIRHA500, MIRHA800, Microwave Incinerated Rice Husk Ash (MIRHA)

I. INTRODUCTION

RICE husk is an agricultural byproduct from rice milling which accounts for about one-fifth of the annual gross rice production of the world [1]. The rice production of South East Asia is about 150M tonnes of paddy per year or 25% of world production, only; 95% of the productions were used within the region and the remaining 5% was exported to other countries [2]. During the milling of paddy, about 78% of weight is received as rice, broken rice and bran while the other 22% of the weight of paddy is received as husk [1]. The Rice Husk Ash, which is developed from the burning of the rice husk at a certain temperature, has been used for cementing material [3] and also has good adsorptive properties. The potential of rice husk ash prepared using different methods have been used in the adsorptive removal of metal ions [4], [5], [6], CO₂ [7] and dye [8]. Microwave Incinerated Rice Husk Ash (MIRHA) which was obtained from burning the rice husk at controlled temperature using microwave incinerator have been studied and can be utilize as alternative adsorbent for removal of metal ions [9],[10]. Heavy metal removals have become one of the major adsorption technology developments. Excessive release of the metals can pollute the environment. Copper is a transition metal that is stable in its metallic state. The effect of toxic copper entering the body may lead to gastrointestinal bleeding, food poisoning (headache, nausea, and diarrhea) [11]. The source of contamination of copper is possibly not

only from copper mining and smelting operation, but also from municipal incineration since copper is hardly found in the source of water [6]. Removal of copper using unconventional adsorbent have been done recently with high value of maximum adsorption capacity, for example 8.92 mg/g using rubber (*Hevea brasiliensis*) leaf powder [12], 58.27 mg/g, hazelnut shell activated carbon[13], 100 mg/g, chestnut shell and 48.98 mg/g, using grape seed activated carbon [14].The aim of this research is to study the feasibility of using MIRHA produced at 500 and 800°C as adsorbent for removal of Cu(II) metal ions from aqueous solutions by using the batch studies. The effect of initial pH, dosage of adsorbent, initial concentration of Cu(II) and contact time between the adsorbate and the adsorbent were studied. The kinetics and adsorption isotherms of Cu(II) were also investigated.

II.METHODOLOGY

A. Preparation and Characterization of MIRHA

Rice husk were collected from BERNAS Rice Mill in Seberang Perak, Malaysia. The rice husk were burned at controlled temperature using a microwave incinerator at 500°C and 800°C to produce microwave incinerated rice husk ash (MIRHA500 and MIRHA800 respectively). Then MIRHA was soaked in 10% hydrochloric acid (HCl) for 24 hours and then washed with distilled water thoroughly to remove excessive acid until the water from the residue reached pH 4. Finally, MIRHA was oven-dried at 103-105°C for 24 hours.The morphology and elemental analysis of the MIRHA500 and MIRHA800 was analyzed using Field Emmision Electron Microscope (FESEM-Supra55VP) with 200x and 1000x magnification.

B. Effect of initial pH at fixed contact time and adsorbent dosage.

The effect of initial pH of the adsorbate on the adsorption of the Cu(II) was studied by varying the initial pH from pH 3 to pH 8. pH adjustment of samples was made using 1N HCl and 1N NaOH. At each pH, 1 g of MIRHA500 was agitated with 100 mL of the adsorbate (aqueous metal solution contain 10 mg/l of Cu (II)) in 250 mL conical flasks. All sampling test were conducted in triplicates. The samples were agitated using the orbital shaker at constant speed of 150 rpm and contact time for 3 hours. At the end of the contact time, the samples were filtered using Whatman No.1 and the filtrates were analyzed for residual Cu (II) concentration using the Atomic Adsorption Spectrophotometer (AAS).

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C. Effect of initial concentration (C_0) and contact time at fixed dosage and pH.

The effect of initial concentration of Cu(II) and contact time on the adsorption of Cu(II) was investigated by agitating separately 100 mL samples of copper solution of initial concentrations 10 mg/L, 50 mg/L and 100 mg/L in 250 mL flasks with 10000 mg/L (1.0 g) of the various adsorbents. The contact times were varied from 0-5 hours with the initial pH set at the optimum pH. Samples were withdrawn at intervals of 30 minutes, filtered using Whatman No. 1 and measured for the residual Cu (II) concentration. All sampling test were conducted in triplicates.

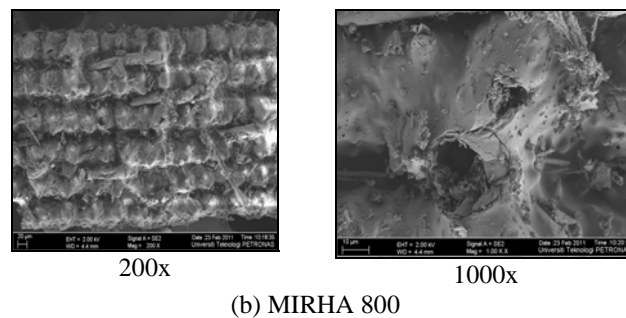
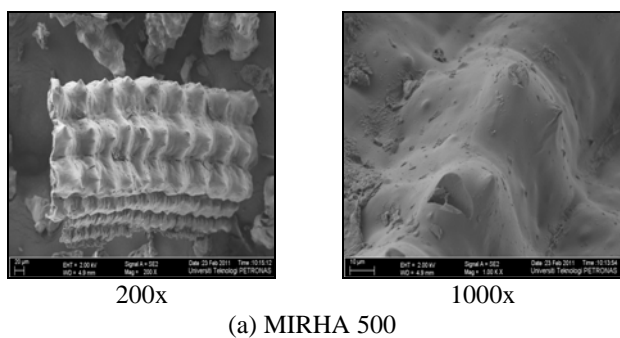
D. Effect of adsorbent dosage and initial concentration at fixed contact time and pH.

The effect of varying the adsorbent dosage on the adsorption of Cu (II) was investigated by agitating Cu (II) solutions with various dosages of MIRHA500. Initial concentration of the adsorbate (aqueous metal solution of Cu(II) were varied at 10 mg /L, 50 mg/L and 100 mg/L. The initial pH of each adsorbate solution was adjusted to its respective optimum pH. The experiment was conducted in triplicates and agitated for 3 hours on the orbital shaker. At the end of the contact time (3 hours), the samples were filtered using Whatman No.1 and the filtrates were measured for residual Cu(II) concentrations.

III. RESULTS AND DISCUSSION

A. Characteristic of MIRHA

Figure 1(a) and 1(b) show the morphology of the MIRHA500 and MIRHA800 at 200x and 1000x magnification, respectively. The morphology of MIRHA500 and MIRHA800 shows beehive structure which can be observed that when the microwave temperature was 500°C, the beehive structure became more prominent (Figure 1a - 200x). It can also be observed that at magnification of 1000x, the surface and ridges of the beehive structure of the rice husk became smoother when it was burned at 500°C. However, when the burning temperature was increased to 800°C, the beehive structure was shattered resulting in more pores being formed on the surface of the adsorbent (Figure 1b - 1000x).



(b) MIRHA 800
Fig. 1 Field Emission Scanning Electron Micrograph of adsorbent at 200x and 1000x magnification, (a) MIRHA500, (b) MIRHA800

The element analysis of the adsorbents MIRHA500 and MIRHA 800 were also analyzed using Field Emissions Scanning Electron Microscopy (FESEM). The results are shown in Table 1 below.

TABLE I
ELEMENTAL ANALYSIS OF MIRHA500 AND MIRHA800

Element	Atomic %	
	MIRHA500	MIRHA800
C	28.52	-
O	56.42	73.44
Si	15.09	35.86
K	0.14	1.68

From the table, it can be observed that at incineration temperature 500°C, the atomic percentage of elemental carbon was lower than at 800°C, all of the elemental carbon was oxidized resulting in an increase in the weight and atomic percentage of elemental silicon and oxygen. It can be concluded that incineration of raw rice at higher temperature will increase the silica content in the adsorbent.

B. Effect of initial pH at fixed contact time and adsorbent dosage.

It can be observed from Figure 2 that as the pH was increased, the Cu (II) removal increased. Above pH6, referring to the metal hydroxide solubility curve [15] Cu (II) starts to precipitate as CuOH₂. Therefore adsorption would be dominant process when pH is less than 6. It also can be observed from Figure 2 that at pH 5, 66% removal of Cu(II) was achieved for MIRHA500 while 71.4% for MIRHA800. It also can be noted that at low initial pH, the removal of Cu(II) is less and vice versa. This happened due to the competition between the H₃O⁺ ion and Cu²⁺ ion to fill the surface of the adsorbent [12].

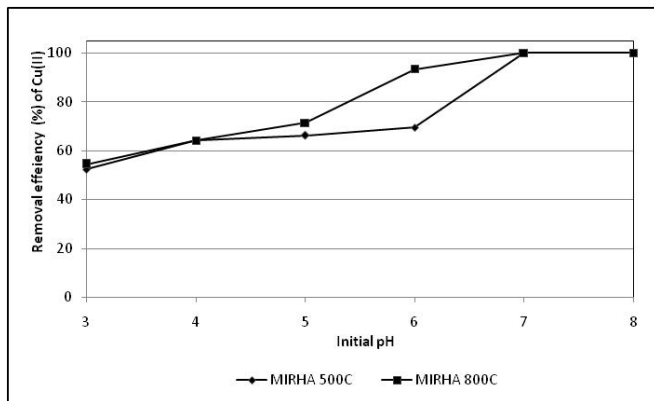


Fig. 2 Removal Efficiency (%) of Cu (II) vs Initial pH for initial copper conc. C_0 at 10 mg/L and 10000 mg/L of adsorbent dosage

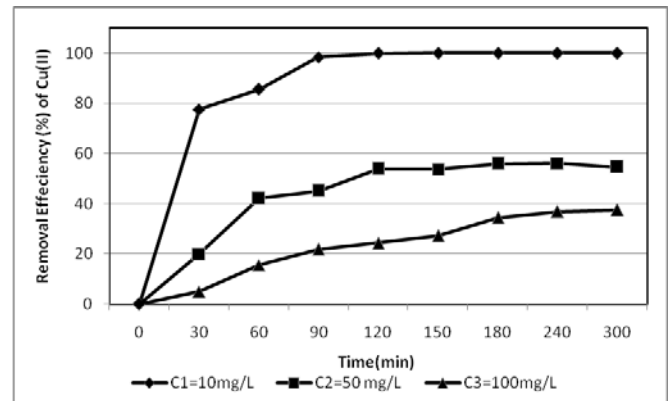


Fig. 4 Removal Efficiency (%) of Cu (II) vs initial copper conc. C_0 at 10 mg/L, 50 mg/L and 100mg/L using 10000 mg/L of MIRHA800

C. Effect of initial concentration (C_0) and contact time at fixed dosage and pH.

The results plotted in Figures 3 and 4 show the removal efficiency (%) of Cu(II) at various initial Cu(II) concentrations. It can be observed from the figures that increasing the initial Cu(II) concentration will decrease the percentage removal of copper uptake onto MIRHA500 and MIRHA800. These happen due to saturation of the adsorbate into the adsorbent and less of binding sites. For initial concentrations of 10 mg/L, 50 mg/L and 100 mg/L the percentage Cu(II) removals of 100 %, 40% and 30 %, respectively for MIRHA500 and 100 %, 50% and 40 % respectively for MIRHA800.

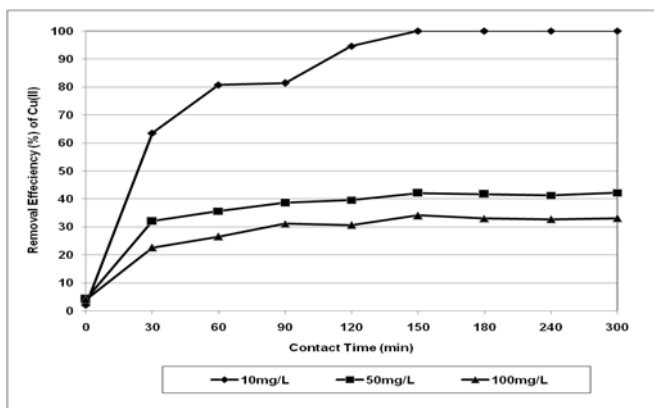


Fig. 3 Removal Efficiency (%) of Cu (II) vs initial copper conc. C_0 at 10 mg/L, 50 mg/L and 100 mg/L using 10000 mg/L of MIRHA500

Figures 3 and 4 also showed that for all initial concentrations, the removal of Cu(II) increase with increasing contact time. For all initial concentration of 10 mg/L, 50 mg/L and 100 mg/L, the saturation point of the adsorbent was achieved after 150 minutes for MIRHA500; while for MIRHA800 the adsorption achieved the equilibrium at 90 minutes, 120 minutes and 180 minutes respectively. This shows quicker adsorption of copper onto the MIRHA500 than MIRHA800.

D. Effect of adsorbent dosage and initial concentration at fixed contact time and pH.

Figures 5 and 6 present the effect of dosage of MIRHA500 and MIRHA800 (0.5 g, 1.0 g, 1.5 g, 2.0 g, 2.5 g and 3.0 g) at initial Cu(II) concentrations of 10 mg/L, 50 mg/L and 100 mg/L. The percentage Cu(II) removal was 100%, 60% and 50%, respectively for MIRHA500 and 100%, 90% and 80%, respectively for MIRHA800. This happened because increasing the adsorbent dosage will increase the adsorption rate due to large surface area and more adsorption site.

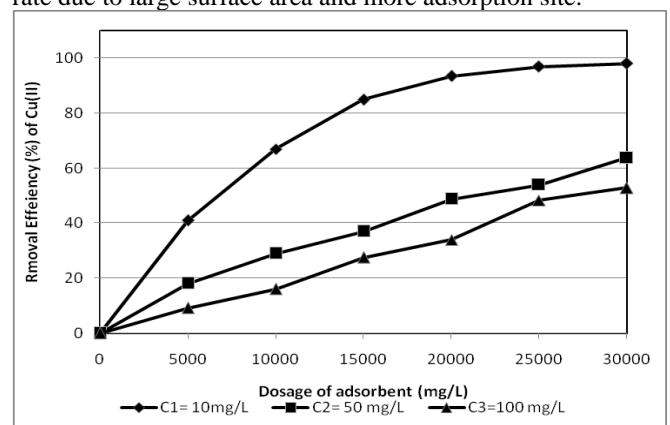


Fig. 5 Removal efficiency (%) of Cu (II) vs various dosage of MIRHA500 for initial copper conc. C_0 at 10 mg/L, 50 mg/L and 100 mg/L and volume of solution is 100mL

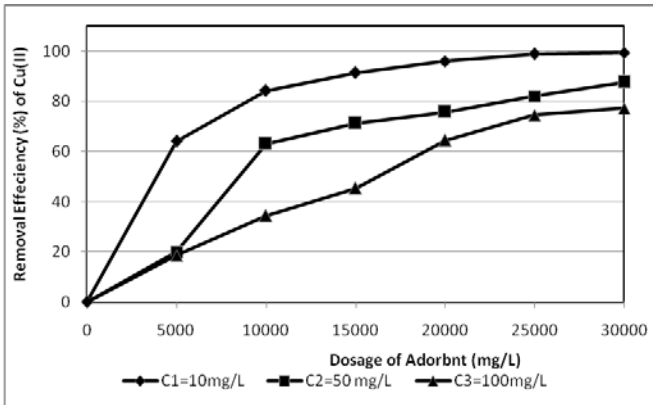


Fig. 6 Removal efficiency (%) of Cu (II) vs various dosage of MIRHA800 for initial copper conc. C_o at 10 mg/L, 50 mg/L and 100 mg/L and volume of solution is 100mL

E. Adsorption Isotherm.

The adsorption isotherms were developed from the data collected. Equilibrium adsorption data were fitted to the linear form of Freundlich and Langmuir's equations (Equation (1) and (2)).

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (1)$$

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \quad (2)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e is equilibrium concentration in solution after adsorption (mg/L), K_f is Freundlich capacity factor, n is the Freundlich intensity factor, Q_0 is adsorption capacity (mg/g) and b is energy of adsorption (L/mg).

TABLE II
LANGMUIR AND FREUNDLICH ISOTHERMS CONSTANTS AND CORRELATIONS.

Adsorbent	Isotherm	Constants and Correlations	
MIRHA50 0	Langmuir	Q_0	3.279
		b	0.045
		R^2	0.504
	Freundlich	K_f	0.456
		$1/n$	0.411
		R^2	0.874
MIRHA80 0	Langmuir	Q_0	3.497
		b	0.185
		R^2	0.939
	Freundlich	K_f	0.820
		$1/n$	0.355
		R^2	0.955

Table II shows that the adsorption of Cu(II) using MIRHA500 and MIRHA800 both satisfies Freundlich isotherm where the R^2 indicate higher value, $R^2 < 0.87$. The Langmuir plot shows that the maximum adsorption capacity for MIRHA500 is 3.279 mg/g and 3.497 mg/g for

MIRHA800. Therefore, it can be concluded that the adsorption of the Cu(II) happens at multilayer surface of MIRHA500 and MIRHA800. This result is similar to the result of the adsorption of cadmium onto the MIRHA[10].

F. Adsorption Kinetics.

The adsorption kinetics can be express as pseudo first order kinetic (3) and pseudo second order kinetic (4) equations.

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where q_e is the amount of solute adsorbed at equilibrium per weight of adsorbent (mg/g), q is the amount of solute adsorbed at time, t , per unit weight of adsorbent (mg/g), K_1 is the first – order constant (min^{-1}) and K_2 is the second – order constant (min^{-1}).

Figure 6 and Figure 7 show the linear plot of pseudo first order kinetic and pseudo second order kinetic models for adsorption of Cu(II) using MIRHA500 and MIRHA800 as adsorbent.

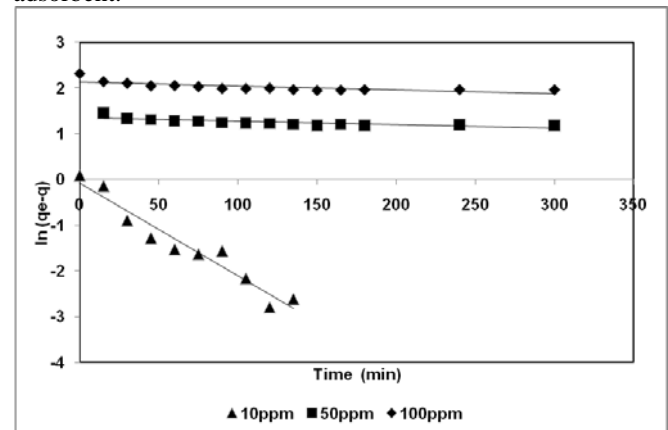


Fig. 7 Pseudo- Kinetic 1st Order of MIRHA500 at different initial concentration 10mg /L, 50 mg/L and 100mg/L 10000 mg/L dosage of adsorbent

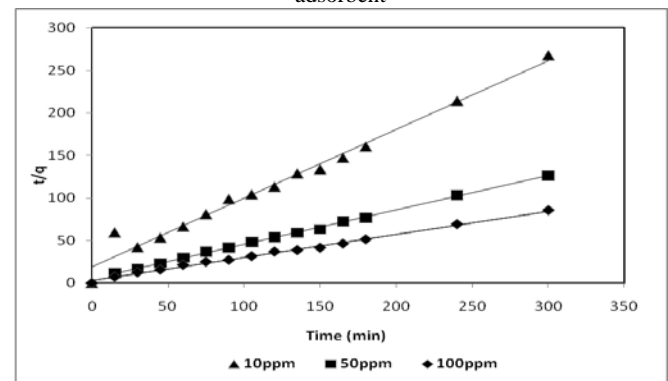


Fig. 8 Pseudo- Kinetic 2nd Order of MIRHA800 at different initial concentration 10mg /L, 50 mg/L and 100mg/L, 10000 mg/L dosage of adsorbent

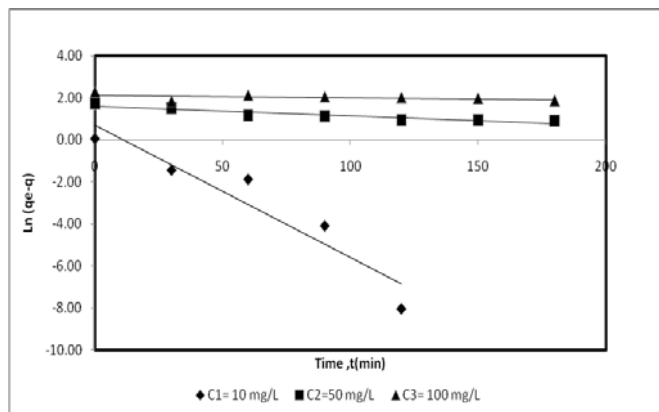


Fig. 9 Pseudo- Kinetic 1st Order of MIRHA500 at different initial concentration 10mg /L, 50 mg/L and 100mg/L, 10000 mg/L dosage of adsorbent

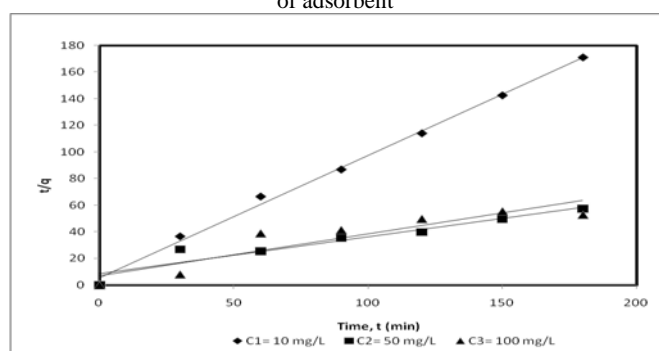


Fig. 10 Pseudo- Kinetic 2nd Order of MIRHA800 at different initial concentration 10mg /L, 50 mg/L and 100mg/L, 10000 mg/L dosage of adsorbent

From Table III, show that the adsorption of Cu(II) into the MIRHA500 and MIRHA800 fits the pseudo-kinetics second order well since the R² values is higher (R²>0.8). It can be assumed that the adsorption of Cu(II) into MIRHA500 and MIRHA800 and both adsorbent applied chemical –sorption or chemisorptions.

TABLE III
KINETICS CONSTANT AND CORRELATIONS.

Adsorbent	Initial Cu (II) concentration. (mg /L)	Pseudo- first order		Pseudo- Second order	
		K ₁ ⁻¹ (min ⁻¹)	R ²	K ₂ ⁻¹ (min ⁻¹)	R ²
MIRHA 500	10	0.021	0.932	0.037	0.982
	50	0	0.9	0.053	0.998
	100	0.001	0.744	0.025	0.988
MIRHA 800	10	0.062	0.896	0.153	0.996
	50	0.004	0.879	0.009	0.913
	100	0.001	0.282	0.014	0.841

From Table III, show that the adsorption of Cu(II) into the MIRHA500 and MIRHA800 fits the pseudo-kinetics second order well since the R² values is higher (R²>0.8). It can be assumed that the adsorption of Cu(II) into MIRHA500 and

MIRHA800 and both adsorbent applied chemical –sorption or chemisorptions.

IV. CONCLUSION

In this study, MIRHA500 and MIRH800 was investigated for its effectiveness in removing of Cu(II) from aqueous solution at different pH, dosage and initial concentration using batch studies and breakthrough performance using column studies. The adsorption best describe Freundlich isotherm using both adsorbent. Both adsorbent also applied chemical –sorption or chemisorptions.

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