ADSORTION CHARACTERISTICS OF Pb(II) ONTO C-4-HYDROXY-3-METHOXYPHENYLCALIX[4]RESORCINARENE IN BATCH AND FIXED BED COLUMN

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Abstract: The adsorption characteristics of Pb(II) cations onto C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarene (CHMPCR) in batch and fixed bed column systems has been conducted. CHMPCR was produced by one step synthesis from resorcinol, vanillin (4-hydroxy-3-methoxybenzaldehyde), and HCl. The synthesis was carried out at 78°C for 24 hours, and afforded the adsorbent in 96,9 % as a 2:1 mixture of C_{4v}: C_{2v} isomer. Most parameters in batch and fixed bed column systems confirm that CHMPCR is a good adsorbent for Pb(II). The adsorption kinetic of Pb(II) adsorptions in batch and fixed bed column systems followed pseudo 2nd order kinetics model. In addition, the adsorption equilibrium isotherm of Pb(II) adsorption in batch system followed Freundlich isotherm. Adsorption capacities of Pb(II) were 5.44 μmol/g (91,84%) in batch system and 3.95 μmol/g in fixed bed column system. Desorption studies to recover the adsorbed Pb(II) were performed sequentially with distilled water and HCl, and the results showed that the adsorption was dominated by chemisorption.

Key words: C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarene, adsorption, Pb(II), batch system, fixed bed column system

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Introduction

Heavy metals are common pollutant found in various industrial effluents. The strict environment regulation on the discharge of heavy metals has led to the necessity to develop various technologies for heavy metal removal. Waste streams containing low-to-medium level of heavy metals are often encountered in metal plating facilities, electroplating, mining operations, fertilizer, battery manufacture, dye stuffs, chemical pharmaceutical, electronic device manufactures, and many others. Most heavy metals are highly toxic and are not biodegradable; therefore they must be removed from the polluted streams in order to meet increasingly stringent environmental quality standards.

Many methods including chemical precipitation, electro-deposition, ion-exchange, membrane separation, and adsorption have been used to treat industrial wastes. Traditional precipitation is the most economic but is inefficient for dilute solution. Ion exchange and reverse osmosis are generally effective, but have rather high maintenance and operation costs and subject to fouling. Adsorption is one of the few promising alternatives for this purpose, especially using low-cost natural adsorbents such as agricultural wastes (maize cob and husk[1], ground pine cone[2]), charcoal[3], fly ash[4], zeolite[5,6], and granular activated carbon[7]. New synthetic adsorbents have also been developed in order to generate alternative materials having different properties compared to those of natural materials.

Calix[4]resorcinarenes are class of synthetic macromolecule having tetramer of resorcine residues in a cyclic array and linked by a methylene bridge. The macromolecules are obtained by acid-catalyzed condensation of resorcinol with a variety of aldehydes. Calix[4]resorcinarenes represent an interesting family of structures which exhibit characteristic of cavity-shaped architecture. Various studies have illustrated their application as host molecules for various guests, such as cations, anions, and molecules. The family of calix[4]resorcinarenes has also been used for various functions, namely as an additive in capillary electrophoresis[8], liquid membrane[9,10], extraction[9], chemical sensing[11,12], and High Performance Liquid Chromatography (HPLC) stationary phase. However, the use of calix[4]resorcinarenes as heavy metal cation adsorbent is still very limited.

C-4-Hydroxy-3-Methoxyphenylcalix[4]resorcinarene (CHMPCR) is calix[4] resorcinarene which has eight benzene residues, twelve hydroxyl groups, and four methoxy groups (Fig 1). CHMPCR was synthesized in this research through acid-catalyzed condensation of resorcinol and vanillin (4-hydroxy-3-methoxybenzaldehyde). The presence of lone-pair electrons in the hydroxyl and methoxy groups, also π-electrons in the aromatic residues can be expected to exhibit characteristics affinities to heavy metal cations, especially Pb(II). The Pb(II) cation is considered to be a intermediate Pearson acid, while CHMPCR with its hydroxyl arms and aromatic rings can form both a “hard” and a “soft” ion binding sites, respectively. Thus, it was of interest to investigate the interaction of CHMPCR with the Pb(II) heavy metal cations.

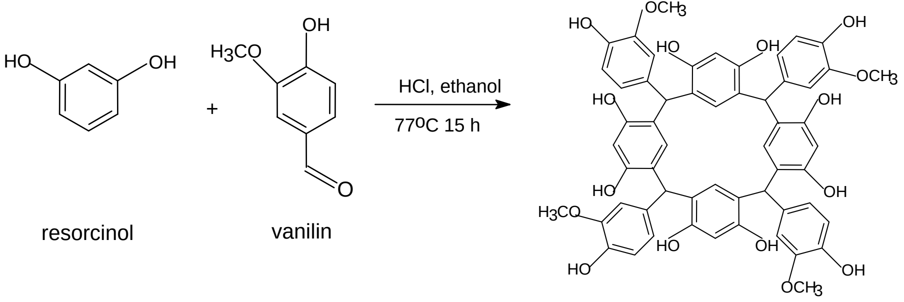

Figure 1. Reaction Scheme of CHMPCR Synthesis

Material and Methods

Reagents

Metal solutions were prepared by diluting 1000 mg/L $Pb(NO_3)_2$ standard solution in aqueous nitric acid to desired concentrations. An adjustment of pH was carried out by adding slowly NaOH and / or HNO_3 solution(s) into the metal solutions followed by stirring until desired pH. Chemicals needed for synthesizing CHMPCR were resorcinol, vanillin, HCl, and ethanol. All materials required were reagent grade from E Merck.

Instruments

In this experiment, equipments involving a set of reflux utilities, buchner funnels, ^1H and ^{13}C NMR spectrometer (Jeol JNM-AL300 FT NMR System, 300 MHz), and FTIR spectrophotometer (Shimadzu FTIR 8201PC) were used for CMPCR synthesizing and characterization. Pump, glass column, stirrer, Atomic Absorption Spectrophotometer (AAS; Perkin Elmer Analyst-100), pH meter (Hanna), were used for adsorption experiment and determination of Pb(II) concentrations.

Synthesis of CHMPCR

Into a solution of resorcinol (0.55 g, 5 mmol) and vanillin (4-hydroxy-3-methoxybenzaldehyde (0.76 g, 5 mmol) in 50 mL of 95% ethanol was added 0.5 mL of hydrochloric acid. The solution was stirred and refluxed at 78°C for 15 hours. The product that separated was filtered. The solid was washed using ethanol-water repeatedly and then dried to give the desired compound as a light purple solid in 96.9% (1.18 g): mp > 390°C (dec), ^1H NMR (300MHz, 298K, DMSO) δ_H: 8.44, 8.36, 8.35 and 7.85 (4 *s*, 12H, ArOH), 6.43-6.08 (*m*, 20H, ArH), 5.45 and 5.40 (2 *s*, 4H, CH methine), 4.39 (*s*, 12H, OCH_3). ^{13}C NMR (300MHz, 298K, DMSO) δ_H: 152.2, 145.8, 143.8, 136.8, 120.9, 120.7, 114.1, 114.0, 102.0, 63.6, 56.0.

Adsorption Procedures

Batch experiment was conducted by adding 0.06 g of CHMPCR (its particle size was < 100 mesh) into 10 mL of metal cation sample solution having concentration about 10 mg/L. The mixture was shaken at room temperature for certain period of time (1 h). The adsorbent was filtered out and dried in a desicator. Concentration of Pb(II) was then measured by AAS. The data obtained was compared and corrected by a blank solution. The blank solution was similar to the adsorption sample except for the existence of the adsorbent. The amount of metal cation adsorbed was calculated from the difference between the metal cation concentration before and after the adsorption experiment. The metal uptake, q (mg metal ion/g CHMPCR) was determined as follows:

$$q = (C_o-C) \text{ x } V/m \qquad (1)$$

Where C_o and C are the initial and the final metal ion concentrations (mg/L), respectively; V is the volume of solution (mL); and m is the CHMPCR weight (g) in dry form. For each metal cation, the experiment was done in 3 conditions, i.e. variation of pH, shaking time, and adsorbent weight.

The fixed bed column adsorption experiment was done in a descendant flow. The equipment used is depicted in Figure 13. The metal solutions were prepared by diluting 1000 mg/L metal cation standard solution in aqueous nitric acid to the desired concentration (10 mg/L). Adjustment of pH of the metal solutions was carried out by adding slowly NaOH and / or HNO_3 solutions followed by stirring until desired pH. This metal solution was passed through the column in a down flow at a fixed flow rate (1 mL/min). The solution which passed through the column was fractionated into 5 cm^3 portions, and the effluent concentration was determined by AAS. Fractions of the effluent were collected until the ratio of effluent concentration (C) to initial concentration (Co) equals to one.

The ratio of C/Co called as breakthrough was plotted against the volume of the solution passed in the column or against the time to obtain a breakthrough curve. The breakthrough time, t_b, was determined as the time when C/Co was equal to 0.05.

Desorption process was done sequentially. Metal adsorbed was eluted with water, followed by aqueous HCl solution at desired flow rate, and 5 mL of fractions were collected. Elution for each desorption agent was conducted until the effluent metal concentration equals to the influent metal concentration.

Results and Discussions

Synthesis and Characterization of CHMPCR

The synthesis of CHMPCR went lovely, easily, and consumed low-cost. The product separated from the reaction mixture at the early minutes of reaction and gave abundance yields as white precipitates. The structure of CHMPCR was confirmed by proton Nuclear

Magnetic Resonance (^{1}H NMR) Carbon Nuclear Magnetic Resonance (^{13}C NMR) and Fourier Transform Infrared (FTIR) spectrometers. It was interesting to note that each signal group in the ^{1}H NMR spectrum emerged as couple of signals having ratio of 2:1. This fact is in accordance with the findings of previous workers[13-16] who found that the products of condensation between resorcinol and aromatic aldehydes were only tetrameric resorcinarenes, and out of four diastereoisomeric products that could theoretically be formed, only two diastereoisomers which were obtained in reality, i.e. C_{4v} (*rccc*, *crown*) and C_{2v} (*rctt*, *chair*). Ratio of C_{4v} and C_{2v} isomeric products varies with the reaction time and temperature.

The interpretation of chemical shifts and the ratios of the amount of the isomers formed were determined through comparison between the proton NMR spectrum of the synthesized CHMPCR and those of the C_{4v} and C_{2v} isomers from reactions products of benzaldehyde and resorcinol which have been separated and fully characterized by previous worker[14]. The two of CHMPCR isomers were identified by four of single peaks for the ArOH (δ_H = 8.44, 8.36, 8.35 and 7.85) having total integration 4.627 according to 12 H, characteristics multiplet signal for the ArH (δ_H = 6.43-6.08) having total integration 12.438 or 20 H, the two of singlet the bridging methine proton signal represent two isomers of CHMPCR (δ_H = 5.45 (C_{4v}) and 5.40 (C_{2v})). Their signals have total integration 1.542 according to 4H, and having ratio integration C_{4v} and C_{2v} isomers 2:1. Finally, a singlet peak for OCH_3 present at δ_H = 4.39 and have integration 4.337 according to 12H.

Interestingly, the crown isomer (C_{4v}) of CHMPCR was present in higher amount compared to the chair isomer (C_{2v}). Hydrogen bonds occurring between adjacent hydroxyl groups and the existence of staggered phenyl groups apparently stabilize the *rccc* crown conformers. In order to avoid a high-cost adsorbent production, the isomeric mixture of CHMPCR was used directly in the metal adsorption experiment. Whereas, the ^{13}CNMR spectrum of CHMPCR presented 11 signals that comes from 11 its carbon type.

The FTIR spectrum of CHMPCR showed characteristics absorption at 3414 cm^{-1} due to O-H stretching vibration. It is well known that absorption bands of O-H stretching vibrations, when free, appear at around 3600 cm^{-1}, and a hydrogen bonding causes these bands to shift to the lower frequencies. The weak frequencies at 2974-2927 cm^{-1} are corresponding to CH stretching frequencies. In addition, the IR spectrum also displayed a significantly intense C-C aromatic streching frequencies at 1612 and 1515 cm^{-1}, CH_3 bending at 1375 cm^{-1} and C-O-C stretching frequency at 1207 cm^{-1}.

Batch System

Effect of pH

The effect of pH on the adsorptions of Pb(II) by CHMPCR was studied in the pH range of 2 to 5 with the initial concentration of metal solution of about 10 mg/L and the results are shown in Figure 2. The amount of Pb(II) adsorbed consistently increased by the increase of initial pH, and it reached optimum value (4.64 μmol/g or 68.42 % in percentage) at initial pH value of 4.

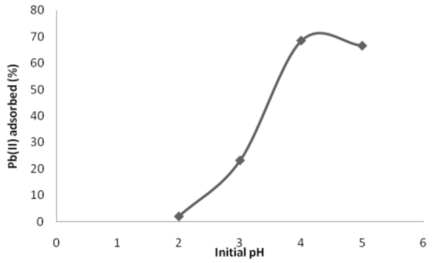

Figure 2. Effect of pH on the adsorptions of Pb(II) onto CHMPCR

The fact that the amount of metal cation adsorbed at low pH was only little apparently was caused by the occurrence of protonation of most donating groups, especially OH groups, of CHMPCR. It was envisaged that the interaction between CHMPCR and Pb(II) cation involved an interaction between oxygen lone pair electrons and metal cation vacant orbitals. As the amount of H^+ at low pH was sufficiently excessive in comparison to that of metal cation, most of oxygen pair electrons perhaps did coordinate with H^+ and not with metal cation. The size of H^+, which is much smaller than that of metal cation, apparently also assisted the occurrence of interaction between oxygen pair electron of CHMPCR and H^+. When the initial pH was sufficiently high (about 4), there was only limited amount of H^+ available in the system. Accordingly, the interaction occurred in the system was dominated by the interaction between oxygen lone pair electron of CHMPCR and metal cation vacant orbital. This is the reason why the amount of metal adsorbed at relatively high pH value was significantly high. However, increasing initial pH to a value higher than 5.0 is not a good idea as there has been decreation of adsorption capacity.

Effect of Contact Time

The result of Pb(II) adsorptions at optimum pH with an increase of contact time is presented in Figure 3. It was found that initially the metal uptake increased as the contact time increased**.**

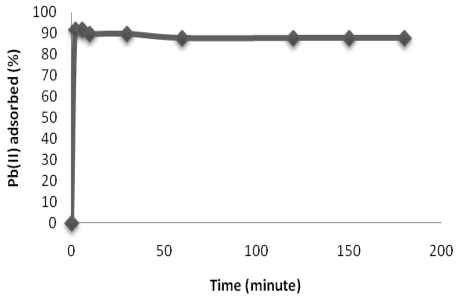

Figure 3. Effect of contact time on the adsorptions of Pb(II) onto CHMPCR

The graph indicates that the Pb(II) adsorption took place quickly at the early minutes of interaction until approximately 6 minutes giving the amount of Pb(II) adsorbed as much as 91.84 % (4.7 μmol/g). It then decreased slowly as the interaction time was extended until reached its constant adsorption value of 87.76 % (4.49

μmol/g) at minute of 60. After interaction process took place during 180 minutes, the amount of Pb(II) adsorbed did not change. Adsorption process at this point has reached equilibrium between the adsorbed metal ions and the free ion in solution**.**

Adsorption Kinetics

The experimental data of contact time effect on the adsorptions of Pb(II) were used for kinetic modeling. The model equations used for fitting the data were: pseudo 1st order (Lagergren) and pseudo 2nd order. The correlation coefficient (R^2) resulted from linear plot of log (q_e-q) versus t, and t/q versus t are shown in Table 1. The adsorption rate constant (k) was calculated using slope or intercept values from the equation, where q_e and q (both in mmol g^{-1}) are the amounts of metal ion adsorbed (metal uptake) at equilibrium and at time t (min), respectively.

Table 1. Kinetic model for Pb(II) adsorptions by CHMPCR in Batch System

Kinetic Model	**R^2**
Pseudo1st order (Lagergren) equation $\log(q_e - q) = \log q_e - (k/2.303)t$	0.6552
Pseudo 2nd order equation $t/q = ½ kq_e^2 + t/q_e$	0.9999

Based on the linear regression values, the kinetics of Pb(II) adsorptions onto CHMPCR could be described well by pseudo 2nd order equation. Thus, it appeared that pseudo 2nd order was the most valid kinetics model.

Effect of Adsorbate Concentration

Figure 4 shows the effect of adsorbate concentrations on adsorptions of Pb(II) onto CHMPCR. The amount of Pb(II) adsorbed consistently increased as the adsorbate concentration increased, and it reached maximum (5.44 μmol/g) at initial adsorbate concentration of 7.92 mg/L, but this value wasn't the optimum value.

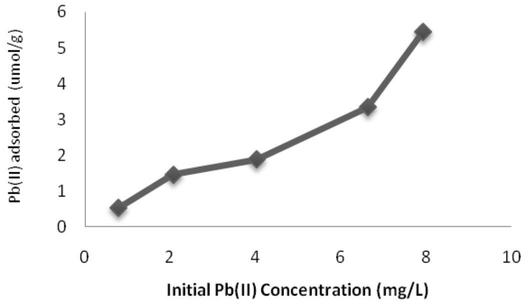

Figure 4. Effect of adsorbate concentration on Pb(II) adsorption onto CHMPCR

Adsorption Isotherms

The equilibrium data in the adsorbtion of Pb(II) onto CHMPCR were analyzed by using Freundlich and Langmuir isotherms, i.e. log q_e = log K + 1/n log C_e and $1/q_e = 1/(K\ q_o.C_e) + 1/q_o$, respectively, where q_e is the amount adsorbed at equilibrium (μmol/g), C_e is the solution concentration at equilibrium (μmol/L), q_o (μmol/g) is the maximum capacity of adsorption, and K is the adsorption constant. The results of linear plots of log C_e versus log q_e (Freundlich model) and $1/q_e$ versus $1/C_e$ (Langmuir model) are shown in Table 2. The K values could be calculated from the slopes and intercepts.

The data on Table 2 shows high values of correlation coefficients (R^2) indicating linear relationships, but R^2 value of Freundlich isotherm was the best. The R^2 values of Pb(II) adsorption were 0.9559 and 0.9110 for Freundlich and Langmuir models, respectively.

Table 2. Estimated isotherm model for and Pb(II) adsorptions

Isotherm Model	**Linier equation**	**R^2**
Freundlich	y=4.3689x+4.7224	0.9559
Langmuir	y=0.4081x-3.3879	0.9110

Fixed Bed Column System

The percentage of metal adsorbed in fixed bed column system is shown in Figure 6. Pb(II) was adsorbed completely (about 100%) at some early fractions until about 3 fractions. This fact showed that CHMPCR can be a good adsorbent for Pb(II). In the next fractions, percent of Pb(II) adsorbed decreased until the column exhausted, i.e. when the effluent concentration equals to influent concentration. This exhausted column took place since 14th fraction.

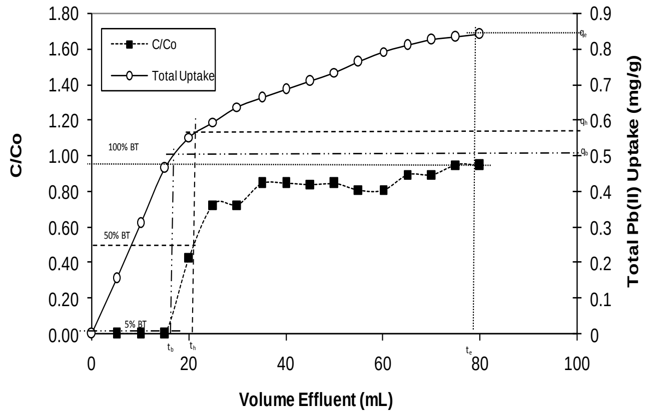

Figure 5. Breakthrough curve adsorption Pb(II) onto CHMPCR

The breakthrough curve of Pb(II) adsorption is presented in Figure 5. It can be seen that 5% breakthrough point (BT), 50% BT, and 100% BT occurred after passing of the feeding solution of about 15, 22 and 75 mL or about 12,5 ; 18 and 62,5 bed volume (BV), respectively.

The column test also showed that the total uptake of Pb(II) (q_e) was 3.95 μmol/g atau 0.46 mg Pb(II) per g of CHMPCR (Figure 7). This value of adsorption column capacity was significantly lower compared to the value of adsorption capacity in batch system that has maximum capacity about 5.44 μmol/g. The initial breakthrough occurred at column loading of about 0.46 mg/g (q_b). This means that the amount of Pb(II) adsorbed has reached 56.7% of the total uptake, although Pb(II) solution applied was only 18.8% of total volume, or 81.2% operating cost would be consumed for taking 44.3% of the rest of Pb(II). Likewise, at C/Co = 0.5, the amount of Pb(II) adsorbed reached almost 70%, i.e. 0.57 mg/g, and consumed as much as 25% of operating cost.

Kinetic Aspect

The kinetics of Pb(II) adsorptions present a shape characterized by strong capacity adsorption during the first few minutes of contact, followed by slow increase until state of equilibrium was reached. As an approximation, the removal of cations can be said to take place in two distinct steps: a relatively fast phase followed by a slower one.

Kinetics of adsorption can be modeled by the pseudo first order Lagergren equation, and the pseudo second order rate equation. The results of linear plots of log $(q_e\text{-}q_t)$ versus t, t/q_t versus t, and $1/(q_e\text{-}q_t)$ versus t are shown in Table 3. The rate constant (k) values can be calculated from the slopes or intercepts according to its equation. According to the data in the table, the pseudo second-order reaction rate model adequately described the kinetics of Pb(II) adsorptions with the highest correlation coefficient.

Table 3. Kinetic model for Pb(II) adsorptions by CHMPCR in Batch System

Kinetic Model	**R^2**
Pseudo First order (Lagergren) $\text{Log } (q_e\text{-}q_t) = \log q_e - kt$	0.9525
Pseudo Second order (Ho) $t/q_t = 1/2kq_e^2 + t/q_e$	0.9868

Desorption

Desorption test was done sequentially to leach heavy metal cations which have been adsorbed onto CHMPCR. This experiment was conducted to recover the column and to estimate the types of adsorption mechanism, hence different solutions was eluted to the column. The principle of this model is the usage of different desorption agents which have desorption ability that increased sequentially, i.e. (1) desorption by water to confirm adsorption mechanism physically (entrapment), (2) desorption by acid solution (HCl), which was used to leach metal cation adsorbed by chemical adsorption via ion exchange or hydrogen bond mechanism.

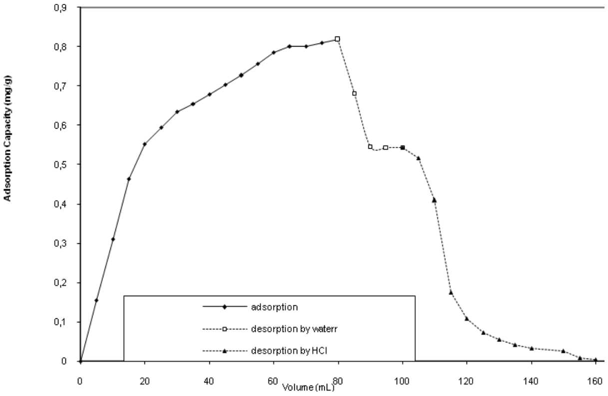

Figure 6. Desorption sequential of Pb(II) on CHMPCR

The result of Pb(II) desorption is performed in Figure 6. According to the graph, water leached Pb(II) about 33.58%, whereas 1 M HCl solution leached Pb(II) completely, up to 99.5%. Based on the data, Pb(II) adsorption by CHMPCR was dominated by chemisorption (more than 66%), but physisorption ruled adsorption mechanism in moderate portion (about 33%).

Conclusions

CHMPCR was produced by one step synthesis from resorcinol, vanillin (4-hydroxy-3-methoxybenzaldehyde), and HCl. The synthesis was carried out at 78°C for 24 hours, and afforded the adsorbent in 96,9 % as a 2:1 mixture of C_{4v}: C_{2v} isomer. Most parameters in batch and fixed bed column systems confirm that CHMPCR is a good adsorbent for Pb(II). The adsorption kinetic of Pb(II) adsorptions in batch and fixed bed column systems followed pseudo 2nd order kinetics model. In addition, the adsorption equilibrium isotherm of Pb(II) adsorption in batch system followed freundlich isotherm. Adsorption capacities of Pb(II) were 5.55 μmol/g (91.84%) in batch system and 3.95 μmol/g in fixed bed column system. Desorption studies showed that the adsorption was dominated by chemisorption.

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