PHOSPHATE REMOVAL FROM WASTEWATER USING CALCIUM SILICATE BY-PRODUCTS DERIVED FROM THE LIENA® PROCESS

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ABSTRACT

Phosphorus is present in soils, sediment, and water in various chemical forms, most commonly as the phosphate (PO₄-3) species. High phosphorus concentrations in aquatic environments may result from agricultural and urban runoff, leaking septic systems, or discharges from sewage treatment plants. Phosphorus abundance can cause eutrophication of water bodies and may lead to algal blooming, which can be toxic to humans and animals. On the other hand, phosphorus is an important nutrient for living cells, but it is a finite resource. Consequently, the recovery and recycling of phosphorus from wastewater for applications such as fertiliser manufacture would be beneficial. This study evaluates the use of calcium silicate by-product (CSB) residue derived from the LieNA® process to remove phosphate from wastewater systems. LieNA® is a novel technology developed by Lithium Australia Limited to extract lithium directly from α-spodumene without the requirement for high-temperature conversion to β-spodumene. XRF, SEM, and TIMA analysis reveal that the CSB residue mostly comprises calcium, sodium, silicon, and oxygen. Phosphate removal experiments using CSB were conducted under a variety of conditions. The CSB showed good adsorption properties for the removal of phosphate from simulated phosphate-containing wastewater. Phosphate removal efficiency was strongly controlled by the dosage of CSB, the initial pH of the solution, and the adsorption time. Phosphate removal efficiency reached 99% after 24 hours adsorption time, at a temperature of 25°C, an adsorbent dose of 20 g L⁻¹, an initial pH of 12, and a 100-rpm stirring speed. The phosphate adsorption had reached equilibrium after 24 hours and the adsorption capacity under these conditions was 4.93 mg PO4-3 per gram of CSB. The data from adsorption kinetic measurements were well fitted by a Lagergren pseudo-first-order model. The phosphate removal efficiency of CSB was compared to that of other calcium compounds, specifically laboratory-grade calcium hydroxide and calcium metasilicate, both of which have been shown to be effective for phosphate removal in previous research studies. The removal efficiency of CSB was only slightly less than that of calcium metasilicate, possibly due to impurities in the CSB, but was ~20% lower than the removal efficiency of calcium hydroxide. The removal of toxic metals was also studied. CSB exhibited 57% removal efficiency for Hg, and the removal efficiency of selected toxic metals (Zn, Cu, Cd, Pb and As) was observed to vary between 10-20% after 24 hours of adsorption time at 25°C, with an adsorbent dose of 5 g L⁻¹, an initial pH of 5, and a stirring speed of 100-rpm. This investigation has demonstrated the potential for using CSB to reduce the concentration of phosphate and toxic elements in wastewater.

Keywords: LieNA® process; Residue; By-product; Adsorption; Wastewater treatment.

INTRODUCTION

Phosphorus is an important mineral nutrient ^[1] for all living things and plays a vital role in the transfer of energy within living cells. It is a major component of nucleic acids (DNA and RNA), teeth and bones and is crucial for cell membranes ^[2,3]. The most common form of phosphorus is phosphate (PO₄) ^[4] and it occurs naturally in the earth's crust, typically in sedimentary rocks and ocean sediments. It can also be found in soil and different types of foods, such as dairy products, meats and poultry, fish, eggs, nuts, vegetables, and grains ^[3,5,6]. Phosphate contributes to the agricultural and industrial sectors, for example, in the production of steel, detergents, rust removers, corrosion preventers, animal feeds, and fertilisers to enhance soil quality for crop growth ^[5,7].

External phosphate inflow into surface water bodies may be a result of agricultural and urban runoff, leaking septic systems, discharges from sewage treatment plants or mobilisation of legacy phosphate ^[8]. Phosphate abundance can cause eutrophication of water bodies and may lead to algal blooming and the growth of invasive aquatic plants, which can be toxic to humans and animals ^[4,9]. It has been reported that eutrophication in an aquatic environment can result in a phosphate concentration between 25 μ g L⁻¹ and 0.03 mg L⁻¹ ^[4]. Consequently, abatement of phosphate inflow into surface water systems is a necessary measure to mitigate and control water eutrophication ^[4,10].

Several investigations have been conducted for the removal and recovery of phosphate from water, including adsorption process, chemical precipitation, advanced biological treatment, electrochemical process, membrane technologies and crystallisation ^[9,11]. Biological treatments such as the conventional activated sludge method can remove 75–100 % of phosphate but are less effective at low phosphate content and require large land areas. A large amount of sludge and waste is produced during phosphate removal by chemical precipitation. Other technologies, such as electrodialysis and reverse osmosis processes are expensive for phosphate removal ^[11].

Adsorption technology is not commonly used on an industrial scale to remove phosphate from wastewater, but it continues to be studied for this purpose due to its simplicity in operation, lower waste generation, significant removal efficiency, environmental friendliness, and low cost ^[11,12].

A number of studies have established that calcium compounds such as $Ca(OH)_2$ (calcium hydroxide), CSH (calcium silicate hydrate) and $CaSiO_3$ (wollastonite) are effective adsorbents for the removal and recovery of phosphate from wastewater streams ^[4,10,13,14,15]. Calcium hydroxide reacts immediately with dissolved phosphate in wastewater and produces calcium phosphate, which then precipitates out of the water ^[13,16].

Wollastonite is a calcium metasilicate (CaSiO₃) material primarily composed of calcium (Ca), silicon (Si) and oxygen (O₂), though a small percentage of impurities (e.g., iron, magnesium, manganese, aluminium, potassium, sodium etc.) can be present ^[16,17]. About 48.3% of the calcium metasilicate is calcium oxide, and this component plays a vital part in the adsorption of phosphate from wastewater systems ^[18].

To date, numerous studies have reported that CSH is a promising adsorbent for phosphate removal and recovery from phosphate-bearing wastewater ^[4,9,10,15,19]. CSH is a semi-crystalline material and chemically represented as CaO₃Si.nH₂O. The composition of CSH is 25% CaO and 30% SiO₂ with a Ca/Si ratio of approximately 1 ^[10]. CSH acts as a seed crystal and the calcium ion donor during the phosphate adsorption process. Simultaneously, CSH also adjusts the pH of the solution which removes the need to add extra chemicals for pH adjustment, thereby increasing the ease of removal of phosphate in the adsorption process ^[9]. Therefore, CSH can be considered a feasible and low-cost adsorbent for phosphate removal from wastewater ^[20]. CSH has been synthesised from various waste products such as alum factory solid waste residue ^[9], carbide residue ^[21], waste glass and shells ^[22], and blast furnace slag ^[23]. Studies ^[9,24,25] have shown that CSH has an ability to adsorb phosphate ions from wastewater systems due to CSH's strong affinity with phosphate ions which produces insoluble calcium phosphate species.

Water contamination by toxic metals is also a serious environmental concern due to the rapid growth of industries and other anthropogenic activities that use or produce these metals ^[26,27,28]. The presence of toxic elements such as copper (Cu), lead (Pb), zinc (Zn), mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr) and nickel (Ni) in water bodies can threaten both aquatic ecosystems and human health ^[27]. Research ^[29,30,31] has reported that CSH can be utilised as an adsorbent to remove toxic metal ions (including Cu²⁺, Cd²⁺, Pb²⁺, As⁵⁺, Zn²⁺, Ni²⁺ etc.) from water.

Inspired by previous research studies, this investigation aimed to investigate the use of the calcium silicate by-product (CSB) residue produced from the LieNA[®] process to remove phosphate from wastewater systems. LieNA[®] is a novel technology developed by Lithium Australia Limited (LIT) to

extract lithium directly from α -spodumene. As per LIT's estimation, about 40% of total waste is generated as calcium silicate by-products (CSB) during the extraction of lithium from α -spodumene using the LieNA® process. Therefore, the reuse of this CSB waste residue for phosphate removal from wastewater, without the requirement of additional chemicals could provide significant economic value add.

This work explored the effect of the phosphate initial concentration, adsorbent dosage, initial solution pH, and contact time on phosphate removal efficiency and adsorption capacity. The phosphate removal efficiencies using each of the calcium compounds Ca(OH)₂, CaSiO₃ and CSB were quantified and compared. Chemical kinetics were investigated in order to obtain the adsorption process mechanism, and the most likely adsorption kinetic model was fitted to the experimental data.

MATERIALS AND METHODS

LieNA[®] Residue Sample

The CSB used in this study was a LieNA[®] residue provided by Lithium Australia Limited, Australia. The LieNA[®] process was developed by Lithium Australia Limited to extract lithium from naturally occurring α -spodumene. This is a less energy-intensive process for extracting lithium from fine spodumene tailings compared to the conventional sulfuric acid method. LieNA[®] is an environmentally friendly process and has the potential to improve sustainability. However, a significant amount of waste residue is produced during this lithium extraction process. **Figure 1** illustrates the flow diagram of the LieNA[®] process and the CSB generating point.

The elemental composition of CSB was analysed using X-ray fluorescence (Bureau Veritas, Australia) and is given below in **Table 1**.

Table 1: Elemental composition of calcium silicate by-product (CSB)

Elements	Са	Si	Na	AI	Fe	Mg	к	Р	LOI
%	21.11	14.14	15.6	0.15	0.06	0.1	0.125	0.034	17.93

Note: The sum of elemental composition does not equal 100 due to the presence of oxygen in the CSB. SEM and TIMA were also used to characterise the elemental and mineralogical composition of the CSB.

CHEMICALS

All chemicals involved in this study were of analytical grade without further purification. The simulated phosphate-containing wastewater samples were prepared from AR grade KH₂PO₄ (potassium dihydrogen phosphate, ChemSupply, Australia). The acid and base solutions used to adjust the initial pH were prepared from AR grade HCI (hydrochloric acid, Rowe Scientific, Australia) and NaOH (sodium hydroxide, ChemSupply, Australia) pellets, respectively. Laboratory grade Ca(OH)₂, (calcium hydroxide, Ajax Fine- chem, Australia) and calcium metasilicate (CaSiO₃, Choice Analytical Pty Ltd, Australia) were chosen for comparison with the phosphate adsorption capacity by CSB. CaSiO₃ was chosen instead of pure CSH due to its restricted supply from chemical providers. High-purity Zn, Cu, Cd, Pb, As and Hg ICP-OES standard solutions (Choice Analytical Pty Ltd, Australia) were used as simulated toxic metals in the wastewater.

PHOSPHATE REMOVAL EXPERMIENTS

A stock solution of phosphate (100 mg L⁻¹) was prepared by dissolving the appropriate quantity of KH_2PO_4 in deionised water. A water bath rotary shaker was used to maintain the temperature during phosphate removal experiments. All phosphate adsorption tests were performed with a continuous stirring speed of 100-rpm.

The effect of the initial pH on phosphate adsorption was investigated for pH values of 3,7,9 and 12 in a 100 mL Erlenmeyer flask at 25°C for 24 hours. The supernatants were filtered, and the residual phosphate concentration in the solutions were measured. The initial pH of the phosphate solution was adjusted using NaOH (0.1 mol L⁻¹ & 1 mol L⁻¹) and HCI (0.1 mol L⁻¹ & 1 mol L⁻¹). The pH was measured by a pH meter (WP-80 handheld pH/mV Meter, TPS, Australia). A dosage of CSB was chosen as 5 g L⁻¹ since the CSB sample quantity was limited, but in addition, Fang et al ^[21] achieved the optimum phosphate removal efficiency with a dosage of 5 g L⁻¹ to 7 g L⁻¹ in 100 mL of simulated wastewater.



Figure 1: Flow diagram of LieNA[®] process showing the CSB generating point (adopted from Lithium Australia Limited).

The effect of each of the calcium compounds $Ca(OH)_2$, $CaSiO_3$, and CSB on phosphate removal was investigated for doses of 1, 5, 10, 15, 20 or 25 g L⁻¹ of each compound. Each dose was mixed with 100 mL of phosphate solution (100 mg L⁻¹) for 24 hours at a temperature of 25 °C. Initially, the pH of the phosphate solution was 4.83 without any adjustment of pH. The separated suspension was filtered. The phosphate concentration in the resulting suspension was determined, and concentration results from all experiments were compared.

After optimisation of CSB dosage and initial pH, the impact of adsorption time on phosphate removal efficiency by CSB was investigated. The parameters for this experiment were 20 g L⁻¹ of CSB in a 100 mL phosphate solution with an initial pH of 12 and a temperature of 25 °C, and the experiment was stopped after 168 hours. Supernatant was collected from the solution at selected times during the experiment, with the first collection occurring at 0.5 hours. The specimen was filtered through a 0.2 μ m filtration membrane, and the residual phosphate and toxic metals concentration in the solution were measured by an inductively coupled plasma-optical emission spectrometer (ICP-OES, Agilent Technologies, Australia).

The phosphate removal efficiency (R_e) and phosphate adsorption capacity of CSB (Q_t) were calculated by the following equations ^[15,19,30].

$$R_e = \{(C_0 - C_t)/C_0\} * 100\%$$

Re = Removal efficiency (%) of phosphate

 C_0 = Initial phosphate concentration (mg L⁻¹) at time t = 0

 C_t = Phosphate concentration (mg L⁻¹) at time t

 $Q_t = \{(C_0 - C_t) V\}/m$

 Q_t = Adsorption capacity (mg g⁻¹)

M = Adsorbent mass (g)

Phosphate adsorption model

Lagergren pseudo-first-order and second-order kinetic models ^[32, 33, 34] were investigated to determine if one of these models closely matched the data from the phosphate adsorption experiments, which would indicate the mechanism for phosphate adsorption on CSB. The Lagergren pseudo-first-order model is expressed in equation (3)

$$dQ_t/dt = k_1 (Q_e - Q_t)$$

3

1

2

Equation (3) can be integrated for the boundary conditions t = 0, $Q_t = 0$ and t = t, $Q_t = Q_t$ to get equation (4):

$$ln(Q_e - Q_t) = ln Q_e - k_1 t$$

where, Q_e and Q_t are the amounts of phosphate adsorbed when the system has reached equilibrium (min) and at time t (min), respectively, and k_1 is the pseudo-first-order adsorption rate coefficient (min⁻¹), which can be obtained from the slope of the linear plot between $ln(Q_e - Q_t)$ and t.

The pseudo-second-order model may be investigated using equation (5)

$$dQ_t/dt = k_2 (Q_e - Q_t)^2$$

Equation (5) can be integrated for the boundary conditions t = 0, $Q_t = 0$ and t = t, $Q_t = Q_t$ to get equation (6):

$$t/Q_t = 1/(k_2Q_e^2) + (1/Q_e)^*t$$

where, k_2 is the second-order kinetic rate constant (min⁻¹), which can be obtained from the inverse of the slope of the linear plot between t/Q_t and $1/Q_e^2$.

TOXIC METAL REMOVAL EXPERIMENTS

The adsorption experiments for selected toxic metals were performed at a temperature of 25 °C with continuous stirring at 100-rpm in a 100 mL (10 mg L⁻¹) conical flask that contained 0.5 g of CSB adsorbent. The toxic metal removal experiment lasted for 24 hours. After this time, a supernatant sample was collected and filtered (0.2 μ m), and the residual concentration of the toxic metals in the sample was then determined using ICP-OES. The removal efficiency (R_e) and the adsorption capacity of CSB (Q_t) were determined using equations 1 and 2.

RESULTS AND DISCUSSION

CSB Characterisation

TIMA (Tescan Integrated Mineral Analyser, Australia) analysis of the CSB revealed that the primary phases were natrite, an O-Na-Ca-Si system and oyelite. A small amount of calcite and wollastonite were also present in the CSB sample. **Figure 2** is the mineral composition map of the CSB for the +500 μ m fractions. 85% of particles in the CSB had a size of <10 μ m.

A CSB sample was prepared and mounted on aluminium stubs and evaluated using SEM to identify the surface morphology (

Figure 3). The energy dispersive spectra (EDS) of the CSB was also observed (Figure 4). The CSB was predominantly composed of sodium, calcium, silicon, and oxygen. Potassium was also detected by SEM-EDS analysis.



Figure 2: TIMA mineral composition map of a CSB cross section showing primary phases present in the sample.

5

6



Figure 3: Optical (a) and SEM (b) images of the CSB sample.



Figure 4 : EDS elemental distribution maps showing the distribution of Na, Ca, Si and K in various grains in the CSB sample.

Phosphate adsorption

Phosphate adsorption at different initial pH values

Typically, the pH value of a solution is an important factor that influences the adsorption of phosphate by a calcium silicate material, as it directly impacts the existence of different species of phosphate such as H_3PO_4 , $H_2PO_4^-$, HPO_4^{2-} ^[9,35,36]. Therefore, it is vital to assess adsorption behaviour of phosphate on CSB in solution with different pH values.

Initial pH values in the range from 3 to 12 were investigated with an adsorbent dosage of 5 g L^{-1} . Phosphate removal efficiency (R_e) and phosphate adsorption capacity (Q_t) calculated from the experimental data are presented in **Figure 5**.

The removal of phosphate from the wastewater system increased as the initial pH value was increased. The highest adsorption occurred in an alkaline condition with a pH value of 12, while the phosphate intake was lowest in an acidic condition (pH = 3). No significant variation in phosphate removal efficiency was observed in a pH range of 7–9. This trend is similar to results from a previous study ^[31] using EMR–CSH as an adsorbent. Other research has also shown that pH is an important factor that determines phosphate adsorption using calcium silicate compounds ^[24,35,37,38,39,40].

The results are potentially due to the existence of different phosphate species in different pH conditions. Phosphate usually occurs as hydrogen phosphate (HPO_4^{2-}) in an alkaline condition, while it exists as dihydrogen phosphate ($H_2PO_4^{-}$) and phosphoric (H_3PO_4) in acidic conditions ^[24,41]. The distribution of various phosphate species at different pH values is shown in Error! Reference source not found. ^[24].

A significant amount of Ca²⁺ ions were released during the adsorption process throughout the entire pH (3-12) range ^[42]. An increase in solution pH (>9) indicates an elution of Ca²⁺ due to the dissolution of calcium silicate material and a simultaneous release of OH⁻ ion ^[42]. As a result, Ca²⁺, OH⁻ and HPO₄²⁻ developed a supersaturated condition and calcium phosphate species ^[43, 44] were precipitated. The solution was unsaturated at low pH (<5) to form potential calcium phosphate species ^[44].

The adsorption reaction can be described by the following equations [9]

$3Ca^{2+} + 2HPO_4^{2-} + 2OH^- \rightarrow Ca_3(PO_4)_2 + 2H_2O$	7
$Ca^{2+} + HPO_4^{2-} + 2OH^- \rightarrow Ca_3(PO_4) OH + 2H_2O$	8

Therefore, the adsorption process may occur at the interface between aqueous phosphate and CSB. The phosphate species replaced the hydroxyl ions on the surface of the adsorbent to create stable, distributed calcium phosphate species.

Phosphorous removal with different calcium compounds and the effect of their dosages

The adsorption process is most economically viable when the highest removal efficiency is achieved at the minimum dosage ^[9]. The effect of dosage on phosphate adsorption removal efficiency was assessed for the commonly used calcium containing materials $Ca(OH)_2$ ^[10] and $CaSiO_3$ ^[18] in addition to CSB.

The adsorbent dosages were increased from 1 g L⁻¹ to 25 g L⁻¹ and the relationships between the dosage of calcium compounds and the removal efficiency of phosphate are shown in **Figure 7**. The results for CSB and CaSiO₃ showed similar trends. The removal efficiency increased as the dosage increased, and the maximum removal efficiency obtained using either CSB or CaSiO₃ was at a dosage of 20 g L⁻¹. However, the removal efficiency for each of these adsorbents at a dosage 25 g L⁻¹ declined slightly. The removal efficiency of CSB was lower than CaSiO₃, possibly due to impurities present in the CSB residue sample. Excellent removal efficiency (99%) was obtained using even a low Ca(OH)₂ dosage of 1 g L⁻¹, and this was maintained for all doses. **Figure 8** shows the adsorption capacity of the CSB in addition to removal efficiency. This decreased significantly for dosages of 10 g L⁻¹ or more, indicating that the full adsorption capacity of CSB is not being used at higher dosages. Based on these results, the dosage of CSB selected for further experiments was 20 g L⁻¹.

Effect of adsorption time

Adsorption time strongly affects the process of adsorption. Therefore, it is essential to evaluate the effect of time on the phosphate adsorption performance using CSB ^[9,21,36,25]. To study the impact of adsorption time on the phosphate removal efficiency of CSB, an adsorption experiment was run with an initial pH of 12, a temperature of 25°C, a CSB dose of 20g L⁻¹, and a 100-rpm stirring speed.

Supernatants were collected at adsorption times between 0.5 and 168 hours, and the residual concentrations of phosphate were determined. Figure 9 illustrates phosphate removal efficiency as a function of adsorption time. The phosphate removal progressed slowly at the beginning of the reaction (0.5 to 2 hours). As a result, the residual concentration of phosphate did not decrease significantly. The removal efficiency rapidly increased from 2 to 24 hours and the maximum removal efficiency of 99.9% was achieved after 24 hours of adsorption. After that, the removal efficiency did not vary until the end of the experiment at 168 hours since the adsorption process had reached an equilibrium. The adsorption capacity of CSB in this experiment was 4.93 mg g⁻¹.

Phosphate adsorption mechanism

Figure 10 and **Figure 11** show equations 4 and 6 for the Lagergren pseudo-first-order model and the Lagergren pseudo-second-order model, respectively, for the adsorption of phosphate on CSB for 30-1440 min at 25°C. The equilibrium rate constant of the pseudo-first-order model (k_1) was estimated to be 00.0088 min⁻¹ and the equilibrium rate constant of the pseudo-second-order model (k_2) was 0.1641 min⁻¹. The pseudo-first-order equation fitted the experimental data better with a correlation coefficient $R^2 = 0.9608$ compared with $R^2 = 0.9286$ for the second-order equation.



Figure 5: Effect of pH value on phosphate adsorption (initial phosphate concentration - 100 mg L⁻¹; adsorbent dose - 5 g L⁻¹; adsorption time - 24 hours; temperature - 25 °C; and stirring speed -100 rpm)



Figure 6: Existence of phosphate species as a function of pH in natural environment ^[24] (α is the distribution co-efficient)



Figure 7 : Effect of different calcium compound's dosage on phosphate removal (initial phosphate concentration -100 mg L⁻¹; initial pH – 4.83; adsorption time - 24 hours; temperature at 25 °C; and stirring speed -100 rpm)



Figure 8: Effect of CSB dosage on phosphate removal efficiency and its adsorption capacity (initial phosphate concentration -100 mg L⁻¹; initial pH – 4.83; adsorption time - 24 hours; temperature at 25 °C; and stirring speed -100 rpm)



Figure 9: Effect of adsorption time on phosphate removal efficiency and its adsorption capacity (initial phosphate concentration -100 mg L⁻¹; initial pH – 12; adsorption time - 24 hours; temperature at 25 °C; adsorbent dose - 20 g L⁻¹; pH - 12).



Figure 10: Lagergren pseudo-first-order kinetics adsorption for phosphorus by CSB.



Figure 11: Lagergren pseudo-second-order kinetics adsorption for phosphorus by CSB.

Toxic metals adsorption

An investigation was carried out to observe toxic element adsorption utilising CSB from simulated toxic metal-contaminated water, as adsorption is one of the most effective ways to remove different kinds of pollutants, including toxic metals, from water ^[45].

The removal efficiency of the selected toxic materials using CSB is shown in **Figure 12** for 24 hours adsorption time, at 25°C. This figure shows the results obtained for Cu, As, Cd, Hg, Pb and Zn. For mercury (Hg), a removal efficiency of $\approx 60\%$ was obtained and the removal efficiencies for other toxic metals (Cu, As, Cd, Pb, Zn) were in the range 10 to 20%.



Figure 12: Removal efficiency of toxic elements using LieNA[®] derived CSB (adsorption time of 24 hours, temperature at 25°C; adsorbent dose of 5 g L⁻¹; and stirring speed -100 rpm)

CONCLUSIONS

This study investigated the adsorptive removal of phosphate from simulated wastewater by CSB, a metallurgical residue generated by the LieNA[®] process. CSB primarily consists of Na, Ca, and Si. It was shown to remove phosphate from wastewater with a high removal efficiency of 99% using an initial phosphate concentration of 100 mg L⁻¹, an adsorption time of 24 hours, a temperature of 25 °C, an adsorbent dose of 20 g L⁻¹ and an initial pH of 12. CSB also showed removal efficiencies of \approx 60% for Hg and 10-20% for Cu, As, Cd, Pb and Zn for simulated toxic wastewater.

This investigation has therefore developed the foundation for an environmentally friendly use of solid LieNA® CSB residue as an adsorbent for wastewater treatment.

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