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Sludge carbonization and activation: From hazardous waste to functional materials for water treatment

Fangwei Cheng[a], Hongxi Luo[a], Lei Hu[b], Bin Yu[b], Zhen Luo[b], Maria Fidalgo de Cortalezzi[c,*]

[a] Department of Chemical Engineering, University of Missouri-Columbia, Columbia, MO 65211, United States
[b] CECEP Both Environment Eng. & Tech. Co., Ltd., Wuhan, Hubei 430071, China
[c] Department of Civil & Environmental Engineering, University of Missouri-Columbia, Columbia, MO 65211, United States

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ABSTRACT

The utilization of sludge from wastewater treatment plants as adsorbent material was investigated. Dry sludge from Ezhou Qingyuan sewage treatment plant (Hubei, China) was heated in anaerobic conditions to produce carbonized sludge, that further chemically activated at higher temperatures and K_2CO_3 to enhance porosity and surface area. The materials were characterized by scanning electron microscopy (SEM), Fourier transformed infrared spectroscopy (FTIR). thermo gravimetric analysis (TGA) and nitrogen adsorption isotherms. TGA curves showed water and low molecular weight organics were lost in a first stage, with the onset of decomposition at 300 °C and up to 700 °C; activation resulted in further carbonization. Nitrogen adsorption experiments yielded Type IV isotherms, characteristic of mesoporous materials. Activation greatly increased surface area, reaching up to 642 m^2/g. FTIR spectra showed the formation of a carboxyl-metal complex at activation, but no further changes in functional groups with increasing reaction temperature. The adsorption capacities of carbonized and activated sludge towards Rhodamine B were investigated by batch and kinetic experiments. Adsorption increased with activation temperature, reaching a maximum at 700 °C with the exception of the sample carbonized at 500 °C where a monotonic increase in capacity was observed. Isotherms showed Langmuir-type behavior; kinetic data was successfully fitted to a pseudo second order model. The adsorption was not affected by pH changes or dissolved solids type and concentration. Zeta potential determinations showed minimal variation of surface charge in the pH range of interest. The results indicated that sludge carbonization is a promising sustainable technology for mass sludge treatment.

1. Introduction

The disposal of sludge from wastewater treatment plants is a major environmental concern worlwide[1]. It contains huge amounts of hazardous pollutants and harmful bacteria, which constitutes a serious threat to the environment and public health when treated ineffectively [1–4] . In China, about 36 million tons of wet sludge (80% moisture) are produced from sewage treatment plants every year, and nearly 60% of it is not treated sufficiently [5–7]. Traditionally, direct landfilling is the main method of sludge disposal [8,9]. However, direct landfilling takes up arable land and increases the possibility of groundwater pollution [8,10]. Alternatively, other methods such as drying and incineration are also employed to stabilize sludge and decrease its volume [11–14]. The amount of sludge is dramatically reduced, but the residue requires further disposal, and landfilling is still necessary. Ash from incineration is another type of hazardous waste and needs to be stabilized using concrete. These strategies are not sustainable, and more environmentally conscious approaches are essential for sludge treatment [8].

Recently, energy recovery and sludge utilization have become a new trend in sludge treatment, which includes the sludge carbonization approach [15–17]. Sludge carbonization is a process where sludge is heated up under anaerobic conditions and transformed into odorless carbon-containing particles [18]. In the late 1990s, sludge carbonization techniques were developed by Japanese companies under the regulations of the Japan Sewage Works Association for emission reduction [19]. By using carbonized sludge as an alternative fuel, emissions were reduced effectively by 23.5–35.8% compared with direct incineration [19,20]. Hence, sludge carbonization has been industrialized,

* Corresponding author.
E-mail address: fidalgom@missouri.edu (M. Fidalgo de Cortalezzi).

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and carbonized sludge is now mainly used as an alternative fuel for power generation in Japan [21].

Compared to raw sludge, carbonized sludge is a better platform to derive sludge based materials since the composition of carbonized sludge is less complicated. Meanwhile, different modification methods can be chosen for carbonized sludge based on its carbon content as well as the target application. Carbonized sludge can be activated to produce activated carbonized sludge with high porosity and surface area [18]. Low-cost, tunable properties, sustainability, and the possibility for mass production make carbonized sludge and activated carbonized sludge promising candidates in fields like air purification and water treatment [22]. The combined sewage system in China, where municipal wastewater is collected with storm wastewater, introduces additional challenges for sludge treatment. The first large scale industrial sludge carbonization system in China was set up by CECEP Both Environment Eng. & Tech. Co., Ltd in 2015, with a capacity of 60 ton dry sludge/day. The carbonized was successfully applied in soil amelioration [23]. However, the specific surface area of carbonized sludge produced was found to be too low to be directly efficiently used as adsorbent material. Compared with the sludge used in some previous works [24], the sludge produced in the plant had a lower organic content (30–40%) [25] and reflects the general situation in China's wastewater treatment plants. Low organic content in sludge brought in challenges in preparation of activated carbon from sludge. As installed capacity for sludge carbonization increases, there is a need to investigate routes for large scale sludge carbonization-activation systems in order to guide the industry level sludge carbonization/activation in China and worldwide. The aim is to advance the sustainability of the wastewater treatment sector providing a safe disposal method for a waste via the conversion into valuable material.

We report in this work a general strategy for large-scale production of activated carbonized sludge from carbonized sludge and apply them in liquid-phase adsorption. The major objectives of this study are (i) to investigate the effects of carbonization temperature on the thermal properties of carbonized sludge and find the optimal carbonization temperature for sequential activation, (ii) to clarify the influence of activation temperature on the specific surface area and pore structures of activated carbonized sludge, and (iii) to evaluate the performance of both carbonized sludge and activated carbonized sludge in liquid-phase Rhodamine B (RhB) removal and to study the interaction between their adsorption differences and porosity. To achieve these objectives, different carbonization temperatures were used to prepare carbonized sludge. For each carbonization temperature, the corresponding carbonized sludge was activated at a different activation temperature to obtain activated samples. Liquid-phase adsorption of RhB was then studied for all samples to assess their performance and collect data for adsorption isotherm and adsorption kinetics. In addition, different conditions such as pH and ionic strength were tested to determine their effects on adsorption. This work presents an approach for massive, sustainable, and low-cost sludge treatment with a focus on application of its products.

2. Experimental methods

2.1. Materials

Sludge was obtained from Ezhou Qingyuan sewage treatment plant (Hubei, China). Ezhou Qingyuan water treatment plant receives storm and domestic wastewater (~95%) and a smaller fraction of pre-treated wastewater from a nearby iron processing plant (5%). The facility includes a 60 t/d sludge carbonization unit on-site.

Prominent properties of the raw sludge and the dry sludge used in this work and corresponding wastewater treated by the plant were summarized in Table 1.

The physicochemical properties of the sludge used in this work were similar to those from Huangshi WWTP (at Huangshi) and Tangxun Lake WWTP (at Wuhan) in the Hubei Province, also listed for comparison in Table 1 as Raw sludge 1 HS and 2 TXL, and thus, it can be considered representative of large WWTPs in China.

Potassium carbonate (K_2CO_3), hydrochloric acid (HCl), Rhodamine B, hydrochloric acid (HCl), sodium hydroxide (NaOH), potassium nitrate (KNO_3), potassium chloride (KCl), potassium sulfate (K_2SO_4), and potassium dihydrogen phosphate (KH_2PO_4) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemical reagents were of analytical grade and directly used as received without further purification. Ultrapure water (18.2 MΩ cm) was obtained in the laboratory and used for the preparation of all solutions.

2.2. Preparation of carbonized sludge and activated carbonized sludge

The synthesis of carbonized sludge and activated carbonized sludge is shown in Fig. 1. The process started at the water treatment plant, with the operations limited by the red line. Firstly, sludge from a secondary settling tank was sent to a storage tank and then pumped into a decanter via a sludge feed pump. Flocculants were introduced at the end of the sludge feed pipeline. Most of the water content in the sludge was removed in the decanter, and further treated at 100 °C for 12 h to obtain absolute dry sludge, which was used in the synthesis of the carbonized sludge and activated carbonized sludge together with the other chemical reagents [27,28].

Table 1
Prominent properties of the wastewater, raw sludge and the dry sludge [25].

	pH	COD (mg/L)	BOD_5 (mg/L)	Total P (mg/L)	NH_3—N (mg/L)	Total Cr (mg/L)	Cr(VI) (mg/L)	Total Cd (mg/L)
Wastewater	7.42	52.6	15.9	0.546	6.999	0.012	0.009	0.001

	H_2O (wt%)	Organic (wt%)	Ash (wt%)	NH_3—N (mg/L)	COD (mg/L)	S_{BET} (m^2/g)	pH
Raw sludge	83	5.2	11.8	N/A	N/A	N/A	N/A
Raw sludge_1_HS [26]	82.4	6.6	11	N/A	N/A	N/A	N/A
Raw sludge_2_TXL [26]	83	6.8	11.2	N/A	N/A	N/A	N/A
Dry sludge	<1	30.3	68.9	27.17	254.48	9.13	6.96

	Cd (mg/kg)	Hg (mg/kg)	Pb (mg/kg)	Cr (mg/kg)	As (mg/kg)	Ni (mg/kg)	Zn (mg/kg)	Cu (mg/kg)
Dry sludge	1.68	0.915	41.6	105	23.9	68.2	731	232
Standard[a]	20	15	1000	1000	75	200	4000	1500

[a] CJ/T 248-2007: The disposal of sludge from municipal wastewater treatment plant – The quality of sludge used for afforestation in gardens or forests; CJ/T: Voluntary Standards issued by the Ministry of Housing and Urban-Rural Development of China.