Production of Activated Carbon from Cow Manure for Wastewater Treatment

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This study presents the chemical compositional analysis of cow manure in terms of holocellulose (35.97%), lignin (19.02%), and ash (17.47%). Activated carbons (of specific surface area 114 to 893 m^2/g, iodine value 219 to 718 mg/g, methylene blue adsorption value 40.5 to 501 mg/g, and ash 16.17% to 22.3%) were prepared from cow manure by using various activator compounds such as potassium carbonate. The results showed that the activation effect of potassium carbonate and zinc chloride was better under the given conditions. The main ash found in the activated carbons was silica, which was reduced to about 3% by washing with sodium hydroxide solution. The prepared activated carbons were used to treat the wastewater from the cow farm and for the pollutant removal that effectively met the discharge standard requirements. These results indicated that the production of activated carbons from cow manure is a promising method for the cleaner production in intensive dairy farms.

Keywords: Cow manure; Bioresource; Activated carbon; Cleaner production; Wastewater

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INTRODUCTION

With the rapid development of the cow breeding industry, intensive, large-scale farming has gradually increased. There are approximately 15 million cows, and the proportion of scale cow breeding (more than 100 cows) reached about 50% in China by the end of 2015 (Gao 2016). Manure quantity obtained from an adult dairy cow is about 30 to 58 kg/day (Guo *et al.* 2013a). Though the development of intensive dairy farms provides high-quality milk for the market, manure and sewage from dairy cow farms is causing increasingly serious pollution to the environment, which hinders sustainable development in the dairy industry. With the improvement of environmental protection requirements, cattle manure can be used in fertilizer, energy (marsh gas), feed (poultry, fish, worms), and cultivation (mushrooms) (Yuan *et al.* 2011; Meng *et al.* 2015). The application of cow manure fertilizer is limited, as excessive mineral elements, veterinary drugs, and other residues present in the manure may degrade soil quality. Biogas production from cow manure by fermentation is a good method, but it is not feasible in Qinghai and other northern China areas because of the low average temperature. Because of the wide distribution of these intensive dairy farms, the yields of cow manure and sewage generated are huge; therefore a variety of reasonable treatments are needed.

Unlike intensive farming, cattle dung is an important fuel for herdsmen in the pastoral areas of the Qinghai Tibet plateau. The chemical constituents of cattle manure are mainly the residues from the consumed plant components that are not completely digested. Activated carbons are effective and widely used as adsorbents because of their developed pore structure and high surface area, and they can be prepared from various biomass or carbonaceous materials. Converting cow dung into activated carbon to treat wastewater is a new way to realize cleaner production in intensive dairy farms. Activated carbons are prepared by chemical or physical methods. Generally, within chemical activation, carbonization and activation take place simultaneously at a lower temperature compared with the physical activation process (Ahmadpour and Do 1997). As the morphology of cow dung is closer to sawdust than to coal or nut shell-like materials, it is more suitable for chemical activation. Potassium hydroxide and phosphoric acid have been used as activators to transform cattle manure into activated carbons (Li *et al.* 2009; Guo *et al.* 2013b). The purpose of this paper is to explore a wider range of activators for cow dung activation and to evaluate the cleaner production in dairy farms.

EXPERIMENTAL

Material

Qinghai Zangditang Biotechnology Co. Ltd. (China) provided cow manure and sewage samples (about 400 cows). Figure 1 shows a typical scene of the dairy farm. The samples of cow manure (Fig. 1d) were ground and sieved to obtain a granulometry of 0.251 to 0.422 mm (40 to 60 mesh) after natural air-drying. All raw material samples were stored in sealed plastic bags.

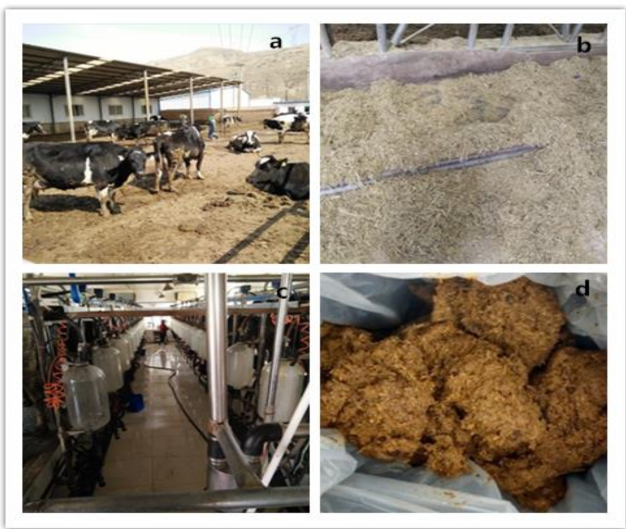

Fig. 1. Qinghai Zangditang Biotechnology Co., Ltd. (a: Dairy farm; b: Cattle feed; c: Milk pumps; d: Cow manure sample)

Analytical grade zinc chloride, calcium chloride, potassium chloride, sodium chloride, magnesium chloride, ferric chloride, manganese chloride, cobalt chloride, copper chloride, potassium carbonate, sodium carbonate, potassium hydroxide, sodium hydroxide, hydrochloric acid, sulfuric acid, nitric acid, sodium thiosulfate, methylene blue, potassium iodide, iodine, soluble starch, potassium dihydrogen phosphate, and sodium hydrogen phosphate were purchased in Tianjin Damao chemical reagent factory (China). All chemicals were used as purchased without further treatment. Deionized water was used for all experiments.

Preparation of Activated Carbons

The impregnation of precursor materials with chemical agents such as $ZnCl_2$ and H_3PO_4 *etc.* can inhibit tar formation and also reduce the volatile matter evolution, resulting in better development of porous structure and high yield of activated carbon products. In order to ensure the effect of impregnation, the activator is usually added in excess (Kilic *et al.* 2012; Alslaibi *et al.* 2013).

Approximately 20 g of cow dung raw material was well blended with an aqueous solution containing 0.44 moles of activator reagent (zinc chloride 60 g, sodium chloride 25.7 g, potassium chloride 32.8 g, calcium chloride 48.8 g, magnesium chloride 41.9 g, ferric chloride 71.4 g, manganese chloride 55.4 g, cobalt chloride 57.1 g, copper chloride 59.2 g, hydrochloric acid 36.7 mL, sodium hydroxide 15.6 g, potassium hydroxide 24.7 g, potassium carbonate 60.8 g, and sodium carbonate 46.6 g). After 24 h of impregnation with the activator reagent, carbonization and activation were carried out simultaneously in a muffle furnace.

The impregnated sample was heated to the activation temperature at a heating rate of 20 °C/min and kept at that temperature for 1 h. After cooling to room temperature, the activated material was washed with hot water 3 times to remove the activator, washed with boiling hydrochloric acid solution ($V(HCl):V(H_2O=1:9)$) for 30 min to remove ash content, and then washed with hot water until the pH became neutral. The activated carbon obtained after the washing was dried in an electric oven at 105 °C for 4 h and then ground thoroughly using a mortar and pestle. The activation processes were performed without any inert gas protection.

Characterization of Activated Carbons

Yield is defined as the final weight of activated carbon produced after activation, washing, and drying processes, divided by initial weight of raw material used on a dry basis.

The ash content, the methylene blue adsorption value, and the iodine adsorption value of samples were determined in accordance with the GB/T 12496.3 (1999), GB/T 12496.8 (1999), and GB/T 12496.10 (1999).

The specific surface area and pore structure parameters of activated carbon samples were obtained from nitrogen adsorption-desorption isotherm determined by a Tristar3000 analyzer (Micromeritics, USA). The specific surface area was calculated according to Brunaue-Emmett-Teller equation (BET).

The ash obtained was characterized with a low vacuum scanning electron microscope X-ray spectrometer (JSM-5610 LV/INCA, Oxford Instruments, England) and XRD (X'pert Pro PANalytical B. V., Netherlands).

Treatment of Wastewater

The main source of sewage in an intensive dairy farm emanates from the cleaning of milk pumps (Fig. 1c). The waste water collected was first filtered with filter paper. Each liter of sewage was treated with 4.0 g of activated carbon and then filtered again. Standard methods (MEPC *et al.* 2002.) were referred for the chemical analyses for suspended solid (SS), chemical oxygen demand (COD), biological oxygen demand (BOD), ammonia nitrogen (NH_3-N), total nitrogen (TN), and total phosphorus (TP). All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

The preparation of activated carbon by chemical activation involves a series of complex reactions occurring at high temperature. The most commonly used activators are potassium hydroxide, phosphoric acid, and zinc chloride. In order to investigate the effect of various activators for the preparation of activated carbon, 14 different compounds including zinc chloride, sodium chloride, potassium chloride, calcium chloride, magnesium chloride, ferric chloride, manganese chloride, cobalt chloride, copper chloride, hydrochloric acid, sodium hydroxide, potassium hydroxide, potassium carbonate, and sodium carbonate were selected. Ten chlorides were selected as activators, the purpose of which was to investigate the effects of different cations. Except for zinc chloride, magnesium chloride, and calcium chloride, the other chloride compounds have not been reported as activators (Saka 2012; Acevedo *et al.* 2015). The choice of carbonates and hydroxides was to comprehensively investigate the role of anions and cations in the chemical activation.

Chemical Constituents of the Raw Material

The characteristic feature of cow dung is its relatively high ash content, which is similar to the composition of rice hull with an ash content of 22% (Mansilla *et al.* 1998). The preparation of activated carbon from rice husk has been reported previously (Zhang *et al.* 2001; Xue *et al.* 2016). The main component of cow dung ash is silica as shown in Figs. 2 and 3.

Table 1. Chemical Constituents of Cow Manure

Component (%)	Moisture	Holocellulose	Lignin	Ash
Cow manure	7.20 ± 0.3	35.97 ± 0.4	19.02 ± 0.2	17.47 ± 0.05

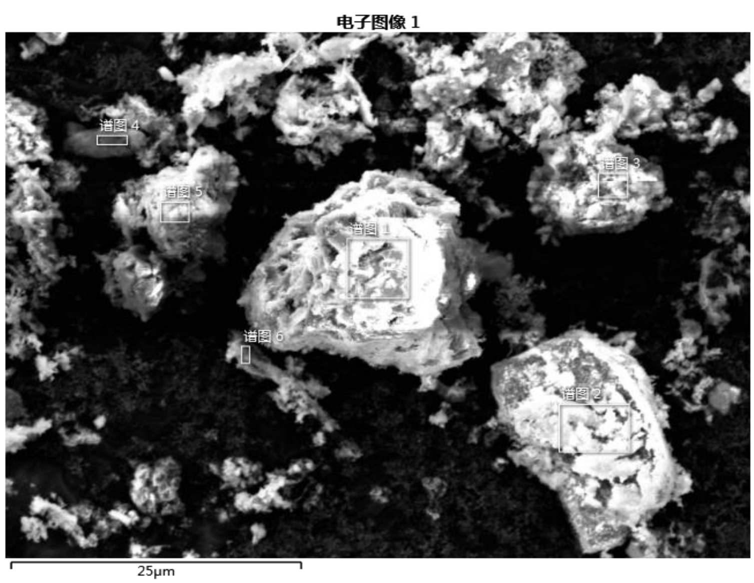

Fig. 2. SEM diagram of ash in cow dung raw materials

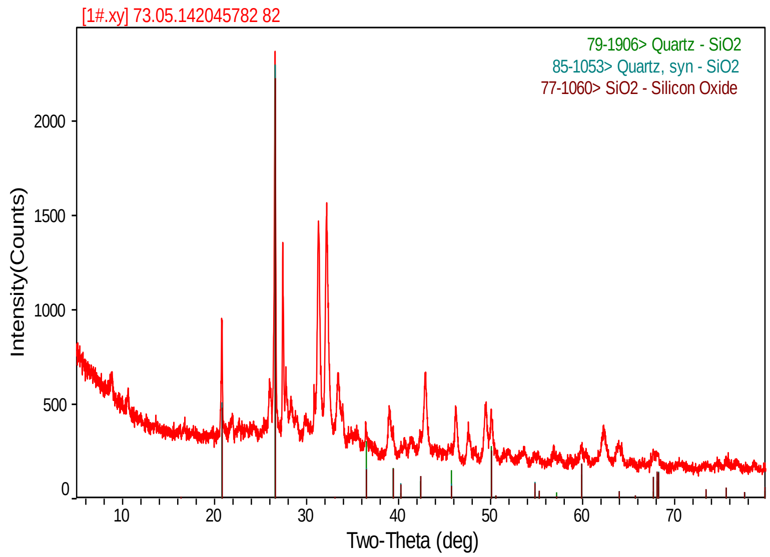

Fig. 3. XRD diagram of ash in cow dung raw material

Table 2. Properties of Activated Carbons Prepared by Different Activators

Activators	Yield (%)	Methylene Blue (mg/g)	Iodine (mg/g)	Specific Surface Area (m^2/g)	Ash (%)
Hydrochloric acid	38.52 ± 1.3	40.5 ± 1.3	308.5 ± 0.5	114.257	20.87 ± 0.3
Sodium chloride	19.84 ± 1.2	93.0 ± 1.4	282.0 ± 0.4	267.050	21.91 ± 0.4
Magnesium chloride	23.98 ± 1.2	151.5 ± 1.6	344.6 ± 0.2	157.474	18.93 ± 0.5
Potassium chloride	24.49 ± 1.5	96.0 ± 1.3	345.2 ± 0.3	124.413	20.75 ± 0.4
Calcium chloride	26.20 ± 1.2	196.5 ± 1.3	470.2 ± 0.2	385.893	19.12 ± 0.3
Manganese chloride	19.75 ± 1.1	133.5 ± 1.5	407.9 ± 0.6	267.343	19.72 ± 0.2
Ferric chloride	22.02 ± 1.4	90.0 ± 1.4	225.3 ± 0.6	137.642	22.30 ± 0.3
Cobalt chloride	17.32 ± 1.4	135.0 ± 1.4	439.1 ± 0.5	485.258	19.52 ± 0.3
Copper chloride	-	-	-	-	-
Zinc chloride	41.50 ± 1.3	202.5 ± 1.4	705.3 ± 0.3	742.517	16.17 ± 0.4
Potassium carbonate	22.47 ± 1.3	501.0 ± 1.3	717.59 ± 0.6	852.692	19.34 ± 0.2
Sodium carbonate	24.75 ± 1.1	103.5 ± 1.5	376.34 ± 0.3	297.458	20.53 ± 0.3
Potassium hydroxide	12.58 ± 1.2	148.5 ± 1.3	466.09 ± 0.4	892.818	22.04 ± 0.4
Sodium hydroxide	7.20 ± 1.3	97.5 ± 1.2	219.44 ± 0.3	284.780	17.46 ± 0.5
*	22.91 ± 0.9	43.9 ± 1.4	335.7 ± 0.5	176.835	33.35 ± 0.5

*Cow dung carbonized at 550 °C

Activated Carbons from Cow Manure

The activation temperature for ten chlorides was 550 °C. It was 750 °C for sodium carbonate and potassium carbonate and 800 °C for sodium hydroxide and potassium hydroxide. The properties of activated carbons prepared by different activators are shown in Table 2.

When the cow dung was carbonized at 550 °C (without activators), the specific surface area of the obtained product reached 177 m^2/g. This value is used as a reference. Hydrochloric acid, ferric chloride, potassium chloride, and magnesium chloride did not have an activation effect under the given experimental conditions. However, when the raw materials was mixed with copper chloride, after activation it turn into ash completely, no carbon containing products were obtained. The overall activation effect of sodium containing compounds was poor (specific surface areas of the products were below 300 m^2/g).

Calcium chloride and cobalt chloride have increased the specific surface area of raw material to a certain extent (385 to 485 m^2/g), and thus indicated the potential as activators, but their activation condition needs further study.

Under the above conditions, the activation effect of zinc chloride was the most prominent among other chlorides, for the highest yield, the best adsorption performance, and the largest specific surface area. The specific surface areas of activated products from potassium carbonate and potassium hydroxide were more than 800 m^2/g. From the experimental results, potassium carbonate appeared to be better than potassium hydroxide. Except for the specific surface area, the yield, methylene blue adsorption value, and the iodine value of the former were higher than the latter.

As shown in Table 2, all products possessed high ash content, which was determined from the high ash content of the raw material itself. The highest ash content of the sample from cattle manure carbonization was obtained due to no pickling and washing. Since the main component of ash is silica, the conventional pickling was not effective. When the samples were treated with hot 20% sodium hydroxide solution for about 1 h, and the ash contents were greatly reduced. The ash contents of the activated carbon samples produced from zinc chloride and potassium carbonate as activators were reduced to 3.27% and 2.15%, respectively.

Wastewater Treatment

For intensive dairy farms, the waste generated every day also included a lot of wastewater, including washing wastewater, milking house cleaning wastewater, and cow urine. For example, Qinghai Zangditang Science and Technology Development Co., Ltd., dairy farm with 400 cows discharged about 9 to 10 tons of waste water per day. A picture of wastewater sample is shown in Fig. 4. The activated carbons prepared from cow manure were used to treat the wastewater produced, and the result is shown in Table 3.

The wastewater treatment process consisted of three steps: filtration, adsorption using activated carbon, and re-filtration. The results of the wastewater treatment with activated carbons by zinc chloride and potassium carbonate reached the discharge standard when the amount of activated carbon used was 4 g/L. Under the same operating conditions, treatment of wastewater with activated carbon from cobalt chloride had greatly improved when compared to the original sewage the sample. But the performance of some activators were not up to the standard used.

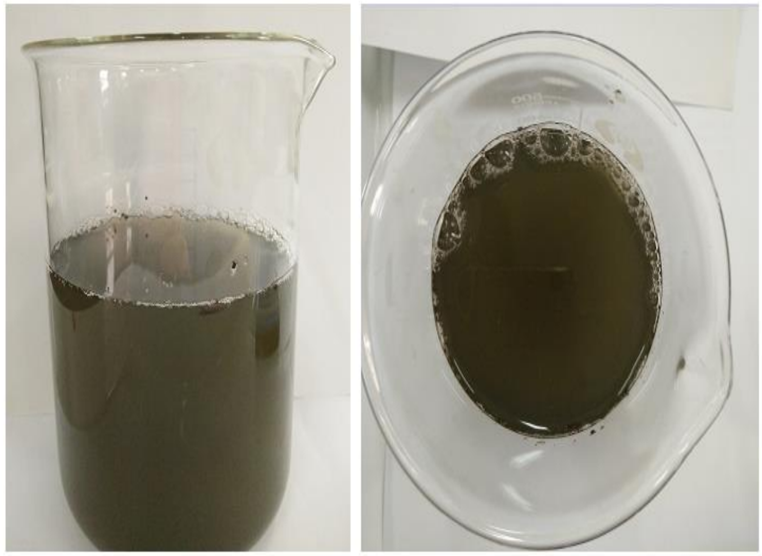

Fig. 4. Wastewater samples from the dairy farm

Table 3. Treatment of Wastewater from Dairy Farm by Activated Carbons

	Original Wastewater	Treated with AC from $ZnCl_2$	Treated with AC from K_2CO_3	Treated with AC from $CoCl_2$	Standard GB-18596 (2001)
SS (mg/L)	163	11	11	12	70
COD (mg/L)	476.4	49.6	50.2	120.6	100
BOD5 (mg/L)	237.4	25.6	22.4	80.5	30
NH_3-N (mg/L)	32.17	9.32	5.18	18.72	25
TP (mg/L)	17.28	2.65	1.77	8.52	3.0
TN (mg/L)	72.31	27.8	21.72	59.4	40
pH	8.74	8.15	8.82	8.22	6-9

CONCLUSIONS

1. Chemical compositional analysis of cow manure indicated holocellulose and lignin as the main components. This result suggests that cow manure can be used as the raw material for the production of activated carbon.
2. Under the given conditions, the activation effects of potassium carbonate, potassium hydroxide, and zinc chloride are the most prominent among the fourteen activators studied. Hydrochloric acid, magnesium chloride, potassium chloride, ferric chloride, and copper chloride showed no activation effect. The activation effects of manganese chloride, sodium chloride, sodium carbonate, and sodium hydroxide were very weak. Cobalt chloride and calcium chloride showed limited activation capacity.
3. The ash content (SiO_2) of cow manure material is large, which leads to higher ash content in the activated carbon products. Compared with the traditional process, if necessary, the production of activated carbon using cow manure should contain an alkaline washing step to reduce the ash content of the products.

4. The activated carbons prepared from cow manure were used to treat the sewage from the cow farm, and thus the water sample can meet the required discharge standard. The treated water can be recycled or discharged. The results indicated that the "zero discharge" from intensive dairy farms is possible. Preparation of activated carbons from cattle manure is thus a promising cleaner production method.

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