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# Simultaneous feces dewatering and antibiotic removal using hydrophobicmodified chitosan flocculants

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Highlights:

Hydrophobic-modified chitosan (MHC) efficiently removes a wide spectrum of antibiotics from feces.

Moisture content of feces is reduced to lower than 60 wt.% after flocculation conditioning and filter pressing.

The combined use of MHC with CaCl2 achieves the best dewatering performance.

Keywords: Hydrophobic-modified flocculants; Feces dewatering; Antibiotics

## **INTRODUCTION**

The large quantities of human feces poses challenges for the environmental and sanitation management, due to the high moisture of feces and the existence of toxic substances such as antibiotics. The dewatering of manure is crucial for reducing the volume of solid waste and easing further treatment and disposal for resource utilization. However, achieving deep dewatering (i.e. moisture content < 60 wt.%) is limited by the hydrophilic nature of extracellular polymeric substances (EPS) and their gel-like structure in feces. Additionally, the presence of antibiotics in feces has emerged as a global public threat if the feces are directly discharged. Therefore, developing suitable treatment methods to simultaneously dewater feces and remove antibiotics are in urgent need.

Flocculation coupled with filter pressing for sludge dewatering has attracted attention with a long history due to its low energy requirements, effectiveness in solid-liquid separation, and relatively low cost in operation. However, flocculation is commonly recognized incapable for removing small-molecular organice substances such as antibioitics. Recently, authors' research group developed a new sorts of flocculants, marked as hydrophobic-modified flocculants (MHCs) by introducing hydrophobic polymeric chains (such as poly(N-alkyl acrylamide)) onto hydrophilic flocculant backbones (such as chitosan), which has been proven efficient in the removal of trace small-molecular organic comtaminants from surface water<sup>[1-5]</sup>. Therefore, in this work, we further assessed the performance of MHC in simultaneously enhancing feces dewatering and antibiotic removal. Under the optimal conditions (HMC dosage: 3 mg/gTSS; CaCl2 dosage: 20 mg/gTSS), the moisure content of feces after flocculation and pressing reduced to 58.3 wt.% and more than 88.7% of AAP were reduced.

### METHODOLOGY

**MHC preparation.** Thiol acetic acid was dissolved in benzene in a flask, heated to 60°C, and nitrogen was bubbled through to remove oxygen. Azobisisobutyronitrile (AIBN) in toluene was then added,















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followed by dropwise addition of N-propylamine (NNPAM) in tetrahydrofuran. The reaction proceeded at 60°C for 6 hours under a nitrogen atmosphere. PNNPAM-COOH was precipitated in ethyl ether, filtered, and obtained. Solid chitosan was dissolved in 1% HCl solution. The pH was adjusted to 5 using a dilute NaOH solution. Activating agents (NHS and EDCI) were dissolved in water and added to the chitosan solution. The reaction occurred at room temperature for 12 hours, followed by precipitation with acetone. The final product, MHC, was washed with ethanol, extracted with acetone for 72 hours, and vacuum dried at 40°C.

**Flocculation and pressure filtration of synthetic feces.** Synthetic human feces were prepared according a previous report[6]. Trace antibiotics (250 ng/g TSS for each) were added into the synthetic feces. Dewatering tests were conducted by a combined process of flocculation (on a Wuhan Meiyu sixplace paddle flocculator; stirring at 200 rpm for 5 min, 100 rpm for 10 min, and 0 rpm for 30 min) and pressure filtration (on a Henan Wanchuan mechanical pressure filter device; at 500 kPa for 30 min). Moisture contents of the dewatered feces were determined by a weighing method. Antibiotic concentrations in the effluent were determined by HPLC-TOF-MS.

### **RESULTS AND CONCLUSIONS**

Feces with initial water content of 84.5% were flocculated using MHC, cationic polyacrylamide (CPAM), CaCl<sub>2</sub>, or the combination of both inorganic and organic flocculants (Fig. 1). For the use of single flocculant, the optimal dosage of MHC (4 mg/g TSS) was significantly lower than that of CPAM or CaCl<sub>2</sub>. Then, when combinedly used with CaCl<sub>2</sub> (20 mg/g TSS), the optimal MHC dosage could be further reduced to 3 mg/g TSS with a better dewatering performance. This will be helpful for the control of cost considering the unit cost of the newly prepared flocculant.

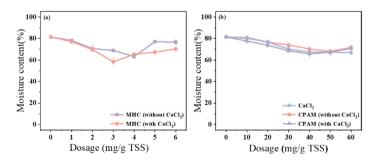


Fig. 1. Moisture contents of dewatered feces as functions of dosages of different flocculants.

Then, removal efficiencies (REs) of trace antibiotics were calculated in the MHC+  $CaCl_2$  system (Fig. 2). REs of different antibiotics were in the range of 60% - 90%, which were significantly higher than the reported REs by flocculation using commercial flocculants (typically < 40%). Among the detected antibiotics, the highest RE of AAP could reach up to 88.7 % whereas TYLwas the most difficult to remove.















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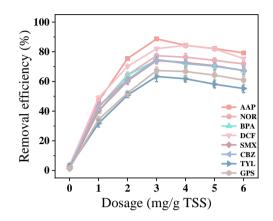


Fig. 2. Removal efficiencies of different antibiotics in the effluent after flocculation-pressure filtration.

Despite the performance, concerns may arise on the cost of the treatment methods. To address this point, two points are to be considered: On the one hand, flocculation method itself has widely used in practical large-scale application for sludge dewatering with affordable cost and proven equipment and facilities; On the other hand, although chitosan and PNIPAM are both environmental-friendly and biocompatible polymers with low secondary pollution risk, processes for large-scale production of the newly developed flocculant MHC are to be optimized in future study in order to further reduce the cost of the flocculant.

On the basis of the results in this work, MHC was proven efficient in the simultaneous feces dewatering and antibiotic removal. As dewatering is an important prerequisite for further reuse of solid wastes, the high dewatering performance by MHC facilitate subsequent treatment and resource utilization of feces.

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