



Enhanced solid–liquid separation of dairy manure with natural flocculants

M.C. Garcia^{a,*}, A.A. Szogi^b, M.B. Vanotti^b, J.P. Chastain^c, P.D. Millner^d

^a Agriculture Technological Institute of Castilla and Leon (ITACyL), Animal Waste Research Line, Carretera de Burgos, Km. 119, 47071-Valladolid, Spain

^b USDA-ARS Coastal Plains Soil Water and Plant Research Center, Florence, SC, USA

^c Dept. of Agricultural and Biological Engineering, Clemson University, Clemson, SC, USA

^d USDA-ARS Sustainable Agricultural Systems and Food Safety Labs, Beltsville, MD, USA

ARTICLE INFO

Article history:

Received 27 June 2008

Received in revised form 10 November 2008

Accepted 11 November 2008

Available online 13 December 2008

Keywords:

Animal waste

Biopolymers

Chitosan

Dairy cow wastewater

Solid–liquid separation

ABSTRACT

The aim of this study was to determine the effectiveness of natural flocculants to reduce solids and nutrient loads in dairy cow wastewater using solid–liquid separation; chitosan was used as a model. Its use efficiency and optimum application rate were determined using flushed dairy cow manure of varied strengths – 0.4%, 0.8%, 1.6%, and 3.2% total solids (TS) content. Treatments consisted of nine rates of chitosan. The flocculated manure was dewatered using 1-mm and 0.25-mm screens. Separation by screening alone was not effective; average efficiencies were about 60% for total suspended solids (TSS), 22% for total Kjeldahl nitrogen (TKN), and 26% for total phosphorus (TP). Mixing with chitosan before screening substantially increased separation. At optimum chitosan rate (0.5 g/L for the highest strength effluent), separation efficiencies were >95% for TSS, >73% for TKN, and >54% for TP. The results of this study indicate that natural flocculants such as chitosan are useful for the solid–liquid separation treatment of livestock wastewater.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

As herd sizes increased over the last few decades, concentration of dairy manure has created potential environmental problems. Most often, the amount of manure nutrients produced exceeds the assimilation capacity of nearby croplands (Nennich et al., 2003). While utilization of dairy manure offers benefits such as increase of soil fertility and quality, improper use can produce air quality and odor concerns and impair water quality.

The US Environmental Protection Agency has found that watersheds with a high concentration of dairy operations have the greatest potential of the major farming types for accelerated eutrophication of nearby surface waters because of the nonpoint source pollution potential of the wastewater (USEPA, 2002). Thus, there is major public interest to develop and demonstrate best control technologies that can lessen or eliminate the disposal problem of large amounts of dairy wastewater.

A simple technology that has the potential to reduce nutrient loads in dairy wastewater is solid–liquid separation. As a pre-storage treatment, solid–liquid separation of dairy wastewater yields separated solids containing organic matter that can be used for compost production or energy generation (Zhang and Lei, 1998). The remaining separated liquid can be used in land application or reused on the farm as flushing water. Solid–liquid separation methods include physical processes such as sedimentation, centri-

fuging, screening, or filtering (Day and Funk, 2002). Usually, solid–liquid separation efficiencies of manure separators are in the range of about 20–68% removal (Burton and Turner, 2003; Chastain et al., 2001). However, separation efficiencies can be augmented by chemical addition of coagulants and flocculants to bind together the small particles of solids into larger clumps (Sievers et al., 1994; Timby et al., 2004; Vanotti and Hunt, 1999, 2002; Zhang and Lei, 1998). Along with the solids, solid–liquid separation combined with flocculation using polyacrylamide (PAM) polymer has been found to separate 85–88% of organic N from the liquid phase (Vanotti et al., 2002, 2005).

Polymer flocculants are macromolecules of varying molecular weights that can have positive, negative or neutral charges (Sievers et al., 1994). These macromolecules destabilize suspended charged particles by building bridges among suspended particles, resulting in newer, larger particles (or flocs) that settle out of the liquid (Vanotti and Hunt, 1999). Flocculants can be divided into three groups: (a) inorganic flocculants such as aluminum sulfate (alum) or polyaluminum chloride (PAC); (b) organic synthetic high-polymer flocculants such as polyacrylamide and polyethylene imine; and (c) naturally occurring flocculants such as chitosan (No and Meyers, 1989), guar gum (J.H. Loughrin, personal communication), sodium alginate (Sievers et al., 1994) and microbial flocculants (Salehizadeh and Shojaosadati, 2001).

Although inorganic and organic synthetic high-polymer flocculants have been most commonly used because of their flocculating effectiveness and low cost, natural organic flocculants may have the advantage over the synthetic ones because they can be produced

* Corresponding author. Tel.: +34 983 31 73 88; fax: +34 983 41 47 80.

E-mail address: GarGonMi@itacyl.es (M.C. Garcia).

economically in large scale and with lower energy input (Salehi-zadeh and Shojaosadati, 2001). In our study, we tested chitosan as a natural flocculant to enhance solid–liquid separation from dairy manure. Chitosan is a natural, biodegradable, nontoxic, polycationic polymer with multiple applications in food, agricultural, pharmaceutical, and chemical industries (Sarkar et al., 2006; Selmer-Olsen et al., 1996; Shahidi et al., 1999; Yamamoto et al., 1995). Chitosan is the deacetylated form of chitin, a polymer found in certain fungi and the exoskeleton of arthropods (Entsar et al., 2003). Commercial chitosan is mostly obtained from chitin found in shrimp and crab shells. Since shrimp and crab shell waste have a production of approximately 10^9 – 10^{10} metric tons of waste per year worldwide, chitin is an abundant natural material for chitosan production (Petter, 1995).

Our objective was to evaluate the effect of wastewater strength on separation of solids and nutrients from flushed dairy manure using chitosan as a natural polymer flocculant. In this work, we determined polymer use efficiencies in flushed manure of varied strength and established optimum polymer addition rates. In addition, to help reduce analytical costs of wastewater management and improve solid–liquid separation process control, we also investigated whether turbidity could be used as a surrogate of expensive laboratory analysis of solids and nutrients.

2. Methods

2.1. Dairy wastewater samples

Dairy manure samples were collected from the Lemaster Dairy Center at Clemson University in South Carolina. The facility included an open-sided freestall, a holding area, and a parlor. The freestalls were bedded with modest amounts of organic bedding (shavings and straw), and the stall and feed area access alleys were flushed once or twice a day. The floors of the holding area and parlor were also cleaned by flushing two or three times a day. All of the rainwater that fell on the roofs and the alleys and the flushed manure from the animal housing facilities and milking center were conveyed to a treatment lagoon by gravity using concrete channels and a large pipe.

Four dairy manure samples with different total solids (TS) content were used to create a range of dairy manure strengths typically found in dairy facilities throughout the USA. Dairy manure with a TS content of 0.4%, 0.8%, 1.6%, and 3.2% was obtained by mixing solid dairy manure and lagoon water. Solid dairy manure was collected with a shovel from the flush alley in the freestall barn. The lagoon water was collected from the flush tank that receives the liquid from the treatment lagoon. Both materials were collected separately in 20-L plastic containers and transported in large coolers filled with ice to the ARS Coastal Plains Research Center in Florence, SC, and kept at 4 °C until mixed in different proportions and used in the bench experiments. Characteristics of the solid dairy manure and treatment lagoon are described in Table 1. Samples of lagoon water collected in the field were transferred into a 100-L vessel and stirred at 150 rpm with a high-torque laboratory mixer to obtain homogeneous samples. A peristaltic pump (Parts 07553-80 and 07017-21, Cole Parmer Instrument Co., Vernon Hills, IL) was used to transfer 8 L of lagoon water sample from the 100-L mixing vessel into four 20-L vessels used to mix the lagoon water and the solid dairy manure. Four different amounts of solid dairy manure were transferred to each 20-L vessel to achieve 0.4%, 0.8%, 1.6%, and 3.2% of TS. Each 20-L vessel was stirred with a high-torque laboratory mixer and 200-mL subsamples were transferred to 250-mL Erlenmeyer flasks for laboratory experiments. Characteristics of the four dairy manure strengths are summarized in Table 2.

Table 1

Characteristics of the dairy manure solids and lagoon liquid that were mixed in different proportions to create the four flushed manure strengths used in the study^a.

Parameters	Solid manure (g/kg) ^b	Lagoon water (g/kg)
Total solids	183.9 (6.4)	2.31 (0.03)
Total Kjeldahl nitrogen	13.00 (0.15)	0.157 (0.010)
Total phosphorus	1.07 (0.01)	0.049 (0.003)
Moisture	816.1 (6.4)	997.7 (0.03)

^a Means (SE), $n = 4$. Solid manure was collected from the freestall alleys using shovels. Lagoon liquid was collected from the surface (0–15-cm depth) of the anaerobic lagoon. Solid manure and lagoon liquid were mixed in various proportions to create flushed manures of various strength typically found in flushing systems for dairy (Table 2).

^b Grams per kilogram of wet solid manure. Concentrations of TKN and TP in solid manure on a dry basis were 16.3 and 5.8 g/kg, respectively.

Table 2

Characteristics of the four dairy manure strengths used for solid–liquid separation.

Dairy manure parameters	Flushed manure strength ^a			
	Low	Medium	High	Very high
Total solids (g/L)	4.6 (0.06)	8.3 (0.38)	16.3 (0.99)	32.2 (2.4)
Total suspended solids (g/L)	2.6 (0.14)	5.3 (0.22)	11.3 (0.50)	28.3 (1.5)
Volatile suspended solids (g/L)	1.6 (0.13)	3.2 (0.14)	6.4 (0.34)	13.8 (0.4)
Chemical oxygen demand (g/L)	3.1 (0.05)	6.5 (0.67)	17.5 (1.5)	29.2 (2.5)
Total Kjeldahl nitrogen (mg/L)	238.6 (3.2)	330.6 (2.9)	456.3 (21)	794.4 (13)
Total phosphorus (mg/L)	70.7 (1.7)	92.7 (1.0)	139.1 (5.23)	236.4 (7.0)

^a Means (SE), $n = 4$. Solid manure and lagoon wastewater samples (described in Table 1) were mixed in different proportions to obtain flushed manure with total solids (TS) concentrations of about 0.4%, 0.8%, 1.6%, and 3.2% (low, medium, high, and very-high strength, respectively).

2.2. Screening and flocculation treatments

Retention of suspended solids and nutrients in flushed dairy manure using screens of various sizes without flocculant addition was performed using dairy manure strength of 1.6% TS. Homogenized dairy manure was passed through nine screens with mesh sizes between 3.360 and 0.250 mm. Screens with mesh sizes of 3.360, 2.000, 1.000, 0.590, 0.500, 0.297, and 0.250 mm were ASTM standard wire screen sieves that corresponded with mesh size numbers 6, 10, 18, 30, 35, 50, and 60, respectively. Screens with 1.588-mm and 0.794-mm opening sizes were stainless steel with round perforations of 1/16 and 1/32 in., respectively, commonly used in commercial screen separators. After screening, recovered liquid samples were analyzed for TSS, VSS (volatile suspended solids), TKN (total Kjeldahl nitrogen), and TP (total phosphorus).

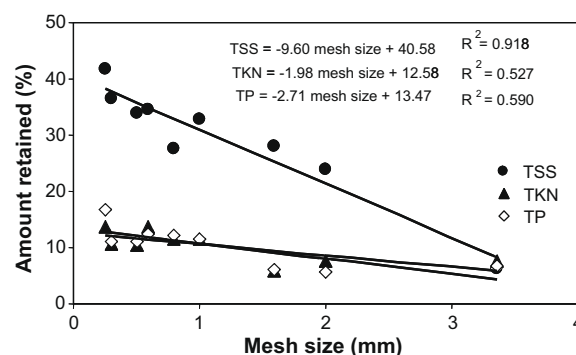


Fig. 1. Retention of suspended solids and nutrients in flushed dairy manure using screens of various sizes. Data are average of two replicate tests performed on high strength dairy effluent (TS = 1.6%, Table 2). TSS = total suspended solids, TKN = total Kjeldahl nitrogen, TP = total phosphorus. Initial concentrations were: TSS = 11.54 g/L, TKN = 570.8 mg/L, and TP = 154.6 mg/L.

Flocculation experiments were carried out using dairy manure with 0.4%, 0.8%, 1.6%, and 3.2% TS content. Chitosan (practical grade supplied by Sigma–Aldrich Inc.) was dissolved in 2% acetic acid (No and Meyers, 1989) for a final concentration of 0.45% (active polymer was not reported). Optimum chitosan dosage was determined using nine polymer rate treatments applied in increments of 60 mg/L in a dosage range of 0–540 mg/L. After polymer application samples were stirred for 1 min and passed through 1-mm and 0.25-mm mesh size screens, the filtered liquid was recovered and analyzed for solids, nutrients, and turbidity.

2.3. Analytical methods

All treated and untreated liquid samples were analyzed according to Standard Methods for the Examination of Water and Wastewater (APHA, 1998). Solids analyses of the liquid samples included

TS, TSS, and VSS. Total solids are the solids remaining after evaporation of a sample to constant weight at 105 °C and include TSS and dissolved solids (DS). Total suspended solids are the solids portion retained on a glass microfibre filter (Whatman grade 934-AH, Whatman Inc., Clifton, NJ) after filtration and drying to constant weight at 105 °C, while VSS is the fraction of the TSS that was lost on ignition in a muffle furnace at 500 °C for 15 min. Therefore, the TSS and VSS are measurements of the insoluble total and volatile solids that are removable by separation. The soluble fraction or dissolved solids was determined by subtracting the TSS from the TS.

Chemical analyses consisted of pH, chemical oxygen demand (COD), ammonia-N ($\text{NH}_3\text{-N}$), nitrate-N ($\text{NO}_3\text{-N}$), TKN, orthophosphate-P ($o\text{-PO}_4$), and TP. For COD we used the closed reflux method (Standard Method 5220D). The inorganic $o\text{-PO}_4$ fraction, also termed reactive P, was determined by the automated ascorbic acid method (Standard Method 4500-P F) after filtration through a 0.45- μm membrane filter (Gelman type Supor-450, Pall Corp.,

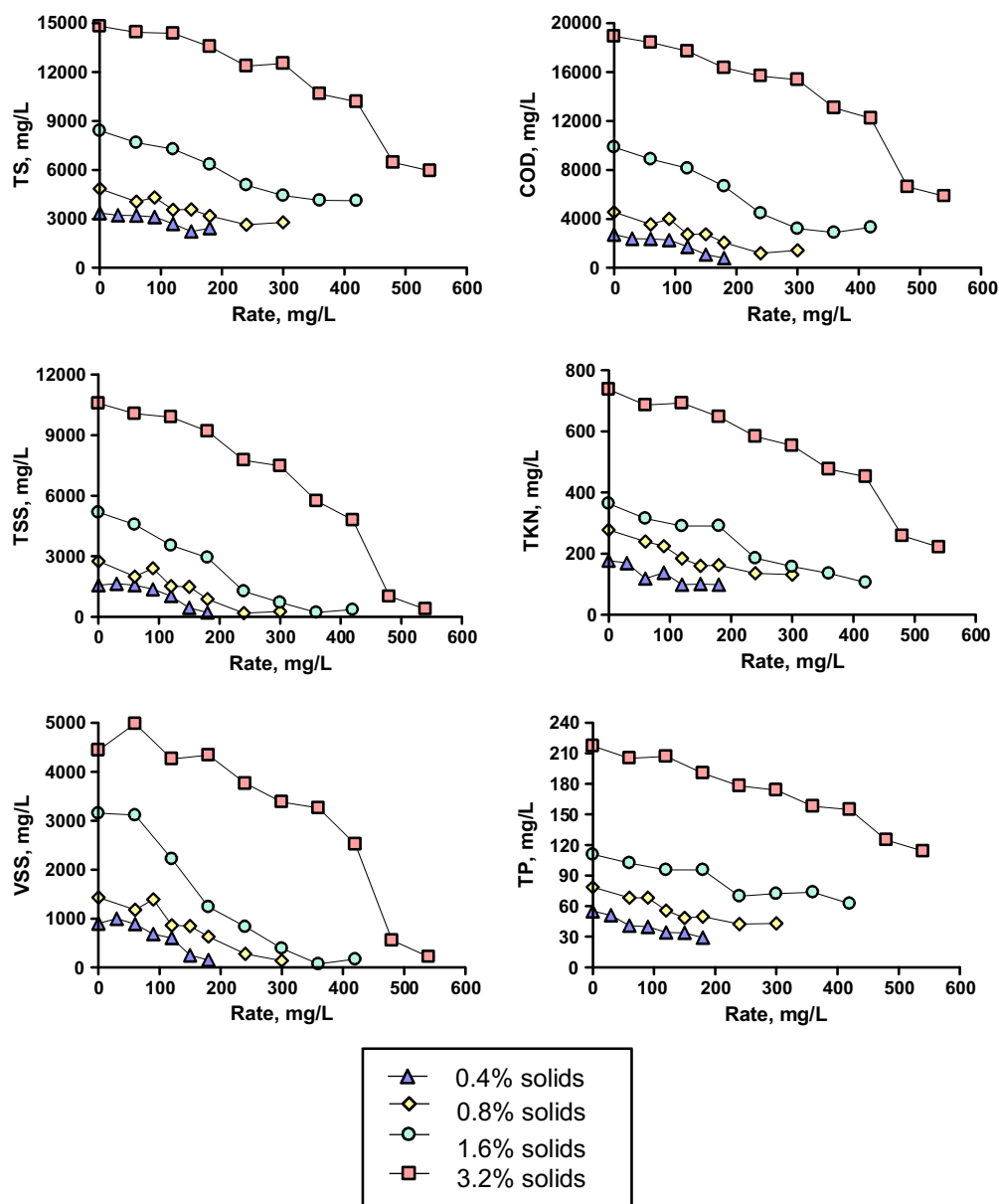


Fig. 2. Removal of solids, COD, and nutrients from liquid dairy manure of various strengths (0.4%, 0.8%, 1.6%, and 3.2% TS) by chitosan flocculation and screening (0.25-mm size screen). Each point is the mean of two replicates.

Ann Arbor, MI). The same filtrate was used to measure $\text{NH}_3\text{-N}$ by the automated phenate method (Standard Method 4500- NH_3G) and $\text{NO}_3\text{-N}$ by the automated cadmium reduction method (Standard Method 4500- NO_3F). The TP and TKN were determined using the ascorbic acid method and the phenate method, respectively, adapted to digested extracts (Technicon Instruments Corp., 1977). The organic P fraction is the difference between TP and o-PO_4 analyses and includes condensed and organically bound phosphates. The organic N fraction is the difference between TKN and $\text{NH}_3\text{-N}$ determinations. Turbidity was measured in the treated effluent by the nephelometric method (Standard Method 2130 B) with a 2100P Hach portable turbidimeter (Hach Co., Loveland, CO) after screening treatment through 1-mm and 0.25-mm mesh size screens.

Solid manure samples were analyzed for moisture content using a microwave moisture analyzer (Omnimark Instrument Corp., Tempe, AZ). Solids samples were dried at 45 °C in a forced-air chamber and analyzed for TKN and TP using the acid block digestion of Gallaher et al. (1976) and the automated methods described before.

2.4. Statistical analyses

Treatment performance was determined by the difference between the solids, nutrient, and COD concentrations in the effluent passing the screen and those in the initial sample before chitosan application and screening. Data were analyzed by means and standard error, and by analyses of variance to evaluate chitosan treatment rate effects (SAS Institute, 1988). Linear and non-linear regression analyses (Draper and Smith, 1981) were used to describe the relationship among measured variables. Non-linear regression analysis that included least square iteration and a Gauss–Newton method (Freund and Littell, 1991) was used to determine linear-plateau functions to estimate optimum chitosan application rates and maximum TSS separation. Both parameters were used to determine TSS removal efficiency and chitosan use efficiency at various dairy manure strengths (Vanotti et al., 2002).

3. Results and discussion

3.1. Removal of solids and nutrients by screening

Homogenized dairy manure samples with a TS concentration of 1.6% were passed through nine screens with different mesh sizes (Fig. 1). Effectiveness of the screening treatment was determined by the difference between the solids and nutrient concentrations in the effluent passing the screen and in the initial sample before screening. Results shown in Fig. 1 indicate that screening *per se* was not highly effective in removing TSS, TKN, and TP. Separation efficiencies were consistently low among the various mesh sizes (<45% for TSS and <20% for both TKN and TP). Several studies on solid–liquid separation of dairy wastewater looked into the retention of suspended solids and nutrients using screens without flocculant addition. Separation efficiencies from our study were lower than those reported by others. A study from Zhang and Westerman (1997) reported 49% of TS removal using a 1.68-mm screen size and influent TS content of 4.6%. Fulhage and Hoehne (1998) obtained removal efficiencies of 45.5% for TS, 17.1% for TKN and 11.0% for TP, using a commercial stationary inclined screen separator with a 1.5-mm screen size. Using the same screen size (1.5-mm), Chastain et al. (2001) reported separation efficiencies of 62.6% for TSS, 49.2% for TKN, and 53.1% for TP in dairy manure and influent TS content of 3.8%. Our lower separation efficiencies results (28% for TS, 5.8% for TP and 6% for TKN and a mesh size screen of 1.588-mm) may be due to the lower TS content of the

dairy manure (1.6%) used in our experiment and the modest amounts of organic bedding used in the freestall at the Lemaster Dairy Center. It has been reported that large solid particles associated with organic bedding and wasted feed increased the fraction of TSS of the flushed manure removed by separators (Chastain et al., 2001). Our results indicate that simple screening was rather ineffective in removing solids and nutrients from dairy manure. Therefore, chemical flocculation was needed to highly reduce TSS and nutrients (N and P) from dairy manure.

3.2. Enhanced solid–liquid separation with chitosan

3.2.1. Reduction of solids

Flocculation experiments were carried out using four different dairy manure strengths: 0.4%, 0.8%, 1.6% and 3.2%, and chitosan as flocculant. The effect of chitosan dosage on average TS, TSS, and VSS concentration at increasing manure strength using a 0.25-mm size screen is shown in Fig. 2. For each dairy manure strength, the optimum chitosan rate dosage necessary for high solids removal efficiency increased with TS content. At optimum dosage, chitosan treatment could remove >96% of TSS and VSS from all dairy manure strengths used in this study.

The effect of chitosan dosage and screen size (0.25-mm and 1-mm) on TSS and VSS removal rates is shown in Table 3 for flocculated liquid dairy manure with 3.2% TS concentration. The highest removal efficiencies were obtained for both TSS and VSS (>98%) using 0.25-mm screening at a chitosan rate of 540 g/L. However, at the same polymer rate of 540 mg/L, these efficiencies were above 95% and 92% for TSS and VSS, respectively, using a 1-mm screen size. This outcome indicates that at optimum chitosan rates the reduction in screen size results in a small improvement in TSS and VSS separation.

Table 3

Removal of total and volatile suspended solids and nutrients from liquid dairy manure strength by chitosan flocculation and screening of 3.2% of total solids concentration and two screens.^a

Removal efficiency (%) ^b				
Polymer rate (mg/L)	TSS	VSS	TKN	TP
<i>0.25-mm screen^c</i>				
0	64.1 (3.0)	67.8 (0.69)	8.3 (5.6)	12.1 (3.2)
60	65.9 (2.8)	63.9 (0.38)	14.8 (3.8)	16.9 (1.9)
120	66.4 (3.0)	69.2 (1.7)	14.0 (3.5)	16.3 (1.1)
180	68.8 (2.6)	68.5 (1.5)	19.6 (2.2)	22.9 (0.06)
240	73.7 (2.4)	72.7 (3.8)	27.6 (1.0)	28.0 (1.0)
300	74.7 (1.5)	75.4 (6.3)	31.3 (0.28)	29.6 (0.59)
360	80.7 (0.4)	76.4 (1.1)	40.7 (2.5)	36.0 (2.5)
420	84.0 (1.0)	81.7 (6.1)	43.8 (5.6)	37.3 (3.9)
480	96.5 (1.5)	96.0 (0.31)	67.9 (1.4)	49.4 (0.31)
540	98.7 (0.3)	98.4 (0.17)	72.5 (0.07)	53.9 (1.2)
<i>1-mm screen</i>				
0	55.9 (3.4)	34.7 (13)	35.7 (10)	39.0 (7.8)
60	54.5 (0.3)	33.3 (7.1)	41.7 (7.6)	42.2 (7.2)
120	54.1 (0.4)	31.9 (7.3)	43.1 (2.8)	43.6 (3.6)
180	56.0 (1.5)	34.2 (5.4)	34.7 (7.0)	33.5 (6.3)
240	57.8 (4.5)	35.7 (0.94)	43.7 (16)	38.0 (13)
300	62.3 (1.3)	44.3 (5.1)	51.0 (2.8)	45.1 (6.1)
360	71.7 (1.8)	57.2 (7.5)	70.8 (6.9)	61.0 (5.0)
420	76.4 (4.4)	65.4 (7.1)	67.1 (3.5)	56.0 (4.9)
480	91.5 (1.2)	85.8 (0.21)	79.9 (11)	56.4 (9.7)
540	95.3 (0.2)	92.3 (0.41)	86.0 (8.1)	61.9 (6.9)

^a Data are means (SE) of two replicate tests performed on very-high strength wastewater (Table 2).

^b Removal efficiency relative to concentration of liquid dairy manure before chitosan treatment and screening. Initial concentrations were: TSS = 28.3 g/L, VSS = 13.8 g/L, TKN = 794.4 mg/L, and TP = 236.4 mg/L.

^c 0.25-mm and 1-mm size screens are ASTM standard wire screen sieves with mesh size numbers 18 and 60, respectively.

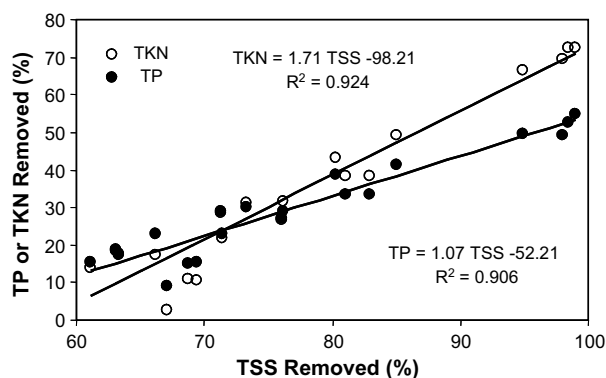


Fig. 3. Relationship between the removal of nutrients and removal of total suspended solids by chitosan treatment and screening (0.25-mm screen size). Data obtained from the dairy effluent of 3.2% strength and nine chitosan rate treatments.

3.2.2. Removal of nutrients

Chitosan treatment followed by screening significantly decreased average TKN and TP concentrations in the effluent at all four manure strengths (Fig. 2). However, reduction of TKN and TP levels in screened liquid was not as dramatic as that observed for TSS and VSS. For instance, chitosan application reduced the TKN and TP concentration on the treated effluent to a maximum of 72% for TKN and 54% for TP using 0.25-mm mesh size screen (Table 3). Lower removal efficiencies for nutrients than for suspended solids were also observed in flocculation of swine manure when using PAM (Vanotti et al., 2002). The inorganic N and P fractions, which are mostly soluble components of TKN and TP, were not affected by the flocculant treatment. On the other hand, PAM was very effective in the capture of organic nutrients contained in small particles. In our study, we found significant, positive linear relationships between TSS vs. TKN ($R^2 = 0.924$) and TSS vs. TP ($R^2 = 0.906$; Fig. 3) that can be explained by the strong affinity between particulate matter and the insoluble fractions of TKN and TP.

3.2.3. Removal of oxygen-demanding substances

The highest removal efficiencies for COD after chitosan treatment and screening (0.25-mm mesh size) of dairy manure with TS strengths of 0.4%, 0.8%, 1.6%, and 3.2% were about 85%, 92%, 88%, and 82%, respectively (Fig. 2). Optimum COD removal efficien-

cies were lower than those obtained for TSS and VSS (Table 4) possibly due to background COD that was not affected by chitosan treatment. Reduced soluble inorganic compounds such as ammonia probably contributed to this background COD (Vanotti and Hunt, 1999). Relationship between effluent COD and TSS removed (data not shown) indicated that 92–99% of COD reduction in the treated effluent was explained by the TSS removal.

3.3. Polymer use efficiency

In order to determine chitosan application rates and maximum TSS separation, a linear-plateau spline function was fitted to data obtained from chitosan treatment and screening through 0.25-mm screen and 1-mm screen; regression parameters are shown in Table 4. The TSS removal rate increased with increasing chitosan dosage reaching an optimum dosage where further increase of chitosan had no effect on suspended solids separation. There is a trend to increase polymer application with the increase of TS concentration independently of the type of screen used to separate solids (Table 4). The same trend has been observed when PAM was used by Zhang and Lei (1998) to flocculate both dairy and swine manure and Vanotti et al. (2002) to flocculate swine manure. Overall, chitosan use efficiency (g TSS separated/g chitosan) for both screening treatments (0.25-mm and 1-mm mesh size) was almost the same (Table 4). On average for both screen sizes, polymer use efficiency increased linearly (from 13.7 to 52.9 g TSS separated/g chitosan) when TSS concentration increased from 4.6 to 32.2 g/L (Pooled polymer efficiency = $1.38TS + 10.17$; $R^2 = 0.981$; $n = 8$).

Optimum polymer rates and TSS removal efficiency were very similar with both screens with an optimum value of 519 mg/L of chitosan for a manure TS content of 3.2% (Table 4). This application rate was within the range of optimum rates of synthetic polymer used for flocculation of dairy manure. Chastain et al. (2001) found an optimum PAM rate of 300 mg/L for dairy manure with 4.18% TS content. Their lower polymer requirement was probably because bedding material particles contained in dairy manure might have improved flocculation performance by trapping small particles and helping floc formation. However, from the study of Zhang and Lei (1998), it was estimated that synthetic flocculant optimum rate could be much higher; their optimum rate was 941 mg/L of PAM for dairy manure with 3.2% TS content.

Table 4
Changes in polymer use efficiency with wastewater strength.

TS conc. (g/L)	TSS conc (g/L)	Regression equations ^a				TSS removal efficiency (%) ^c	Polymer use efficiency ^d (g solids/g polymer)	Polymer usage rate ^e	
		R ^{2b}	Slope (g/mg)	Optimum chitosan rate (mg/L)	Max. TSS removed (g/L)			(%)	(lb/ton)
0.25-mm screen									
4.6	2.65	0.973	0.0123	176.8	2.42	91	13.71	7.29	145.8
8.3	5.34	0.965	0.0154	222.3	5.11	96	22.98	4.35	87.02
16.3	11.32	0.975	0.0169	317.8	11.02	97	34.68	2.88	57.68
32.2	28.30	0.954	0.0339	518.8	27.90	99	53.78	1.86	37.19
1-mm screen									
4.6	2.65	0.987	0.0144	173.0	2.36	89	13.64	7.33	146.6
8.3	5.34	0.991	0.0121	240.1	4.86	91	20.24	4.94	98.80
16.3	11.32	0.993	0.0248	294.0	10.41	92	35.41	2.82	56.48
32.2	28.30	0.974	0.0413	518.9	27.03	96	52.09	1.92	38.40

^a Linear-plateau functions: $Y = a + bX$ for $X < \text{knot}$, and $Y = \text{plateau}$ for $X > \text{knot}$, where $Y = \text{TSS removed (g/L)}$, $X = \text{chitosan rate (mg/L)}$, $a = \text{intercept}$, $b = \text{slope}$, $\text{knot} = \text{optimum chitosan rate}$, and $\text{plateau} = \text{maximum TSS removed (based on Vanotti et al., 2002)}$.

^b R^2 = coefficient of determination; all values significant at the 0.05 probability level.

^c TSS removal efficiency = $\text{max TSS removed}/\text{initial TSS concentration}$.

^d Polymer use efficiency calculated from parameters of regression equations ($\text{maximum TSS removed}/\text{optimum chitosan rate}$).

^e Polymer usage rate given both in percent (g chitosan/100 g dry solids separated) and lb/ton (lb polymer/2000 lb dry solid separated).

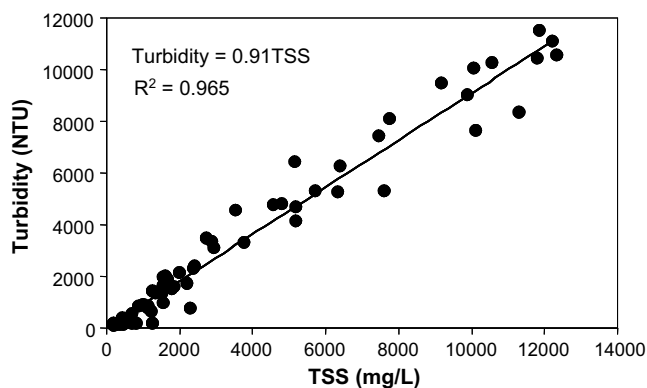


Fig. 4. Relationship between effluent turbidity and total suspended solids (TSS) concentration after chitosan treatment and screening. Data include four dairy wastewater strengths (TS = 0.4%, 0.8%, 1.6%, and 3.2%), seven to nine chitosan rates (0–540 mg/L), and two mesh size screens (0.25 and 1 mm). Each point is the mean of two replicates.

3.4. Turbidity relationships – process control

The performance of a wastewater treatment plant can be determined by suspended solids measurement, but laboratory analysis is necessary. An indirect method for suspended solids measurement is turbidity, which can be quickly measured on-site. In our work, flocculation performance was also determined by changes in turbidity. As Fig. 4 shows, high correlation ($R^2 = 0.965$) was obtained between turbidity and TSS after chitosan and screening treatments (0.25-mm and 1-mm mesh size screens). The relationship between TSS and turbidity indicates that turbidity measurement can be used as a TSS removal performance indicator in a wide TSS range (from 0.4% to 3.2% TSS content). Sievers et al. (1994) found similar results between turbidity and VS for dairy manure with 1% TS content, concluding that turbidity measurement was a good method to determine maximum solids removal and optimum chemical dosages. An additional advantage of using turbidity measurements to assess performance of polymer enhanced solid–liquid separation is its strong relationship with effluent nutrient concentration such as concentration of TP. Fig. 5 shows the relationship between effluent TP and effluent turbidity after polymer and screening treatment. Turbidity measurement is cheaper and quicker than TP analyses, thus routine estimation of nutrient concentrations from turbidity measurements can reduce laboratory analyses cost.

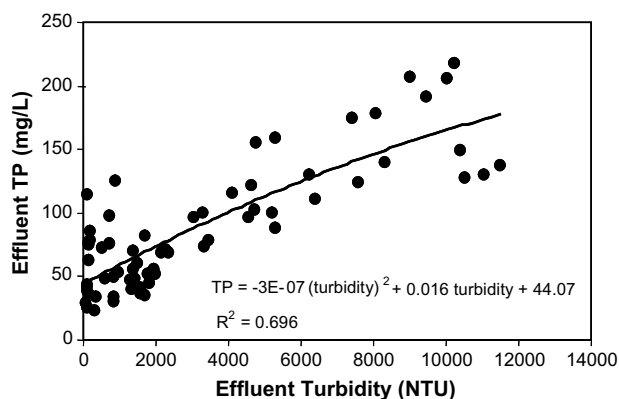


Fig. 5. Relationship between effluent total phosphorus (TP) and turbidity after chitosan flocculation and screening. Data include four dairy wastewater strengths (TS = 0.4%, 0.8%, 1.6%, and 3.2%), seven to nine chitosan rates (0–540 mg/L), and two mesh size screens (0.25 and 1 mm). Each point is the mean of two replicates.

4. Conclusions

Organic nutrients in dairy manure are mostly contained in the solid fraction that cannot be efficiently separated by simple mechanical screening. Since the modern farming trend towards large operations leads to a surplus of nutrients in nearby cropland, there is a need for better distribution of these nutrients. Solid–liquid separation of livestock effluents enhanced by flocculant addition is a good option to concentrate these nutrients in the separated solids and easily transport them for land application or other uses such as composting or bioenergy production.

Our interest was to test if natural flocculants can have a role in effective solid–liquid separation of livestock effluents. We showed that chitosan, a natural flocculant, can greatly improve the efficiency of dairy manure solid–liquid separation and improve the water quality of the treated effluent. At optimum rate of the flocculant, removal efficiencies were >95% for total suspended solids (TSS), >73% for total Kjeldahl N, and >54% for total phosphorus (TP). These removal efficiencies were comparable to those reported in the literature for dairy manure treatment using synthetic polymers.

Because of increased cost of energy and renewed interest on organic farming systems, natural flocculants such as chitosan have the potential to be used as a component of animal waste treatment. Natural flocculants may have an important role in organic farming because the manure solid fraction separated using these flocculants could be considered an organic fertilizer as it does not contain synthetic compounds. Future research on natural flocculants for use in animal manure treatment should be focused on: (1) development of new natural flocculants and (2) cost effective production of natural flocculants.

Acknowledgements

This research was part of USDA-ARS National Program 206: Manure and Byproducts Utilization; ARS Project 6657-13630-003-00D “Innovative Animal Manure Treatment Technologies for Enhanced Environmental Quality.” The first author, Dr. M.C. Garcia, is grateful to Drs. M.B. Vanotti and A.A. Szogi for providing the opportunity to work as a Visiting Scientist in the USDA-ARS, Coastal Plains, Soil, Water and Plant Research Center at Florence, SC. The authors are grateful to April Q. Ellison for her help with laboratory analyses. Mention of a trade name, proprietary product, or vendor does not constitute a guarantee or warranty of the product by the USDA and does not imply its approval to the exclusion of other products or vendors that also may be suitable.

References

- APHA, 1998. Standard Methods for the Examination of Water and Wastewater, 20th ed. American Public Health Association, American Water Works Association, and Water Environment Federation, Washington, DC.
- Burton, C.H., Turner, C., 2003. Manure Management: Treatment Strategies for Sustainable Agriculture. Silsoe Research Institute, Bedford, UK.
- Chastain, J.P., Vanotti, M.B., Wingfield, M.M., 2001. Effectiveness of liquid–solid separation for treatment of flushed dairy manure: a case study. *Appl. Eng. Agric.* 17, 343–354.
- Day, D.L., Funk, T.L., 2002. Processing manure: physical, chemical and biological treatment. In: *Animal Waste Utilization: Effective Use of Manure as a Soil Resource*. Lewis Publishers, Boca Raton, FL, pp. 243–282.
- Draper, N.R., Smith, H., 1981. *Applied Regression Analyses*. John Wiley and Sons, New York.
- Entsar, I.R., Mohamed, E.B., Christian, V.S., Guy, S., Walter, S., 2003. Chitosan as antimicrobial agent: applications and mode of action. *Biomacromolecules* 4, 1457–1465.
- Freund, R.J., Littell, R.C., 1991. *SAS System for Regression*, 2nd ed. SAS Institute, Inc., Cary, NC.
- Fulhage, C.D., Hoehne, J.A., 1998. Performance of a screen separator for flushed dairy manure. In: Chastain, J.P. (Ed.), *Proceedings of the Fourth International Dairy Housing Conference*. ASAE, St. Joseph, MI, pp. 130–135.

- Gallaher, R.N., Weldon, C.O., Boswell, F.C., 1976. A semiautomated procedure for total nitrogen in plants and soil samples. *Soil Sci. Soc. Am. J.* 40, 887–889.
- Nennich, T., Harrison, J.H., Meyer, D., Weiss, W.P., Heinrichs, A.J., Kincaid, R.L., Powers, W.J., Koelsch, R.K., Wright, P.E., 2003. Development of standard methods to estimate manure production and nutrient characteristics from dairy cattle. In: Ninth International Animal, Agricultural and Food Processing Wastes Symposium Proceedings. ASAE, St. Joseph, MI, pp. 263–268.
- No, H.K., Meyers, S.P., 1989. Crawfish chitosan as a coagulant in recovery of organic compounds from seafood processing streams. *J. Agric. Food. Chem.* 37, 580–583.
- Peter, M.G., 1995. Applications and environmental aspects of chitin and chitosan. *J. Macromol. Sci. Pure Appl. Chem.* 32, 629–641.
- Salehizadeh, H., Shojaosadati, S.A., 2001. Extracellular biopolymeric flocculants. Recent trends and biotechnological importance. *Biotechnol. Adv.* 19, 371–385.
- Sarkar, B., Chakrabarti, A., Viyaykumar, A., Kale, V., 2006. Wastewater treatment in dairy industries – possibility of reuse. *Desalination* 195, 141–152.
- Shahidi, F., Arachchi, J.K.V., Jeon, Y.J., 1999. Food applications of chitin and chitosans. *Trends Food Sci. Technol.* 10, 37–51.
- Selmer-Olsen, E., Ratnaweera, H.C., Pehrson, R., 1996. A novel treatment process of dairy wastewater with chitosan produced from shrimp-shell waste. *Water Sci. Technol.* 34, 33–40.
- SAS Institute, 1988. *SAS/STAT User's Guide*, Ver. 6.03. SAS Institute, Inc., Cary, NC.
- Sievers, D.M., Jenner, M.W., Hanna, M., 1994. Treatment of dilute manure wastewaters by chemical coagulation. *Trans. ASAE* 37, 597–601.
- Technicon Instruments Corp., 1977. Individual/simultaneous determination of nitrogen and/or phosphorus in BD acid digests (dialyzer). Industrial method 337-74W/B. Technicon Instruments Corp., Tarrytown, NY.
- Timby, G.G., Daniel, T.C., McNew, R.W., Moore Jr., P.A., 2004. Polymer type and aluminum chloride affect screened solids and phosphorus removal from liquid dairy manure. *Appl. Eng. Agric.* 20, 57–64.
- USEPA, 2002. The benefits of reducing nitrate contamination in private domestic wells under CAFO regulatory options. EPA-821-R-03-008. US Environmental Protection Agency, Office of Water, Washington, DC.
- Vanotti, M.B., Hunt, P.G., 1999. Solids and nutrient removal from flushed swine manure using polyacrylamides. *Trans. ASAE* 42, 1833–1840.
- Vanotti, M.B., Rashash, D.M.C., Hunt, P.G., 2002. Liquid–solids separation of flushed swine manure with PAM: effect of wastewater strength. *Trans. ASAE* 45, 1959–1969.
- Vanotti, M.B., Rice, J.M., Ellison, A.Q., Hunt, P.G., Humenik, F.J., Baird, C.L., 2005. Solid–liquid separation of swine manure with polymer treatment and sand filtration. *Trans. ASAE* 48, 1567–1574.
- Yamamoto, H., Amaike, M., Saito, H., 1995. Biodegradation of chitin, chitosan, and cross-linked chitosan gels by microorganisms. *Biomimetics* 3, 123–139.
- Zhang, R.H., Lei, F., 1998. Chemical treatment of animal manure for solid–liquid separation. *Trans. ASAE* 41, 1103–1108.
- Zhang, R.H., Westerman, P.W., 1997. Solid–liquid separation of animal manure for odor control and nutrient management. *Appl. Eng. Agric.* 13, 657–664.