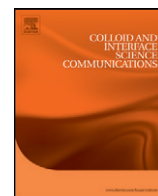


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Rapid Communication

Direct Relationship Between Electrokinetic Surface-charge Measurement of Effluents and Coagulant Type and Dose

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ABSTRACT

Colloidal stability due to rejection between particles with identical charge is a severe problem in water treatment. Pretreatment of industrial effluents such as olive mill or cowshed dairy wastewater includes the addition of “coagulants” aimed at neutralizing the colloids and reducing their rejection. However, the amount and type of coagulant are usually determined by “trial-and-error” jar tests due to the lack of an efficient method to evaluate the effluents' charge. This study presents a method for direct evaluation of the efficiency of type and dose of coagulants based on particle charge detector (PCD) measurements of the colloidal effluents and the coagulant to be used as the neutralizing compound. This presumably trivial procedure is not common, apparently due to the fact that measuring colloidal charge with a PCD is less widely used than ζ potential measurements. A few examples of the effective use of this procedure are presented.

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Colloidal stability (i.e., colloids' tendency to remain dispersed) in organically loaded effluents is ascribed to three effects [1]: (a) small particle size, yielding large hydrodynamic friction forces; (b) electrostatic repulsion due to similar charges of the effluents' colloids, which keeps the particles in suspension, and (c) the density of the organic colloids, which is close to that of water and therefore, even if a large neutral particle forms, its sinking velocity will be very slow. In wastewater, colloid removal is crucial to avoiding clogging of aerobic or anaerobic digesters. The first step in this process is a stage technically known as “coagulation”, defined as neutralization of the colloids' charge, thereby reducing the electrostatic repulsion between them and enabling their aggregation. In some cases, this process is followed by “flocculation”, in which bridging compounds are used to form chemically bonded links between the neutral colloidal particles, enmeshing them into relatively larger masses [2].

The literature related to wastewater treatment describes a clear relationship between the ζ potential and colloidal stability: high absolute values of ζ potential are related to stable dispersions, whereas values

close to zero are related to neutralization, yielding coagulation which in turn enables flocculation [3,4]. The ζ potential is defined as the difference in electrical potential between the shear plane of a colloidal particle and the bulk of the solution, and it is commonly employed to evaluate flocculation potential [5]. In some publications on water treatments, it is stated that if the ζ potential is large, then more coagulants are needed. However, without negating the usefulness of ζ -potential measurements, it is entirely possible that a surface can have an inherent charge but no measurable ζ potential and vice versa [6,7]. For example, olive mill wastewater (OMW) usually has a very low absolute ζ potential (ca. -10 to -20 mV) compared to nonpolluted stream water (ca. -200 to -300 mV), but the amount of electrolyte needed to neutralize OMW's potential is 50- to 500-fold higher than that for stream water (Rytwo and König, 2012 unpublished results). The ζ potential is an “intensity” parameter, whereas in some cases the total charge—a “capacity” parameter—is needed. As an analogy, consider the difference between pH (as an indicator of acidic “intensity”) and buffer capacity (a “capacity” parameter indicating how much base is needed to neutralize an acidic solution).

Another electrokinetic technique is based on a streaming current detector (SCD), first introduced by Gerdes in 1966 [8]. This technique, applied in a “particle charge detector” (PCD) instrument, has been devised to measure the amount of electrokinetic surface charge directly by combining an electrokinetic SCD probe with titration of a charge-compensating polyelectrolyte. The technique is relatively simple and

Abbreviations: NTU, nephelometric turbidity unit; OMW, olive mill wastewater; PCD, particle charge detector; PD, polyDADMAC, polydiallyldimethylammonium chloride; RCF, relative centrifugal force; SCD, streaming current detector; TSS, total suspended solids.

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Table 1
Charge, TSS and turbidity of olive mill wastewater (OMW; initial charge of $-1900 \mu\text{mol L}^{-1}$) treated with increasing amounts of coagulant (a 2.5% suspension of NC21Z with an initial charge of $+89,000 \mu\text{mol L}^{-1}$).

Final concentration of NC21Z [ppm]	Volume of NC21Z suspension added		Effluent turbidity after treatment		Measured effluent charge		NC21Z evaluated added charge		Evaluated remaining charge of OMW	
	mL	L^{-1}	NTU	NTU	$\mu\text{mol L}^{-1}$	$\mu\text{mol L}^{-1}$				
0	0		973		-1900	0				-1900
100	4		305		-1400	356				-1544
200	8		146		-1000	712				-1188
300	12		88		-650	1068				-832
500	20		28		-180	1780				-120
750	30		120		450	2670				770
1000	40		278		1300	3560				1660

requires no additional model assumptions [9]. The principle of charge measurement is based on the generation of a streaming potential which is induced by the oscillating movement of a plunger in a polytetrafluoroethylene cell, while gold electrodes placed in the cell record the electrokinetic signal. The surface charge is then quantified by titration with charge-compensating polyelectrolytes. Addition of the titration solution is performed across the point of zero charge, i.e., the point at which the electrokinetic surface charge measured by the SCD is zero [10]. This instrument has been used for several applications, for example, to monitor the influence of pH on clays [11] or the amount of modifier on modified clays [12], and recently, to measure the specific charge of superplasticizer samples in water/cement pore solutions [13].

This study presents a direct evaluation of the efficiency of various types and doses of coagulants based on PCD measurements of the colloidal effluents and the coagulant to be used as a neutralizing material. The suggested procedure aims to simply equalize the charge of the colloidal effluents and that of the added coagulant [14]. In general it includes:

- Measuring C_e , the concentration of charges in the effluent in $\text{mol}_c \text{L}^{-1}$ by performing polyelectrolyte titration with the PCD instrument. C_e might be negative or positive depending on the effluent.
- It is obvious that if the effluents are negatively charged, a cationic coagulant should be used, and an anionic coagulant should be used for positively charged effluents. After choosing a suitable coagulant, it is subjected to PCD measurement, which yields C_c , the concentration of charges in the coagulant in $\text{mol}_c \text{L}^{-1}$.
- The volume of coagulant (V_c) needed to neutralize a given volume of effluent (V_e) is simply calculated by the ratios: $V_c/V_e = |C_e/C_c|$.

The absolute value of the charge ratio is needed, since the effluent and coagulant charges have opposite signs.

The above-described procedure was tested in OMW which had been pretreated in an anaerobic digester. The outflow was very rich in colloidal material (total suspended solids (TSS) = 1600 mg L^{-1} , turbidity = 973 NTU). Coagulation was performed with increasing doses of a 2.5% suspension of NC21Z, a coagulant based on nanocomposites comprised of 0.8 g polyDADMAC (PD) per g sepiolite clay [14,15].

The use of fibrous clay for the preparation of nanocomposites might seem puzzling at first, since layered structured minerals (montmorillonite, illite) offer a larger interaction area between the mineral and the polymer. It should be considered that for water treatment a relatively low viscosity fluid is needed in order to be able to easily administrate the coagulant suspension to the effluents. Montmorillonite-PD nanocomposites were tested and worked efficiently, but to avoid formation of a dense non-flowing gel, clay concentrations were kept only 40% of those achieved with sepiolite. Coagulants could only be prepared with a maximum of about 0.5 g polymer per g clay, whereas in sepiolite nanocomposites, values could reach 2.5 g polymer per g clay [14]. Indeed, Galan [16] mentions that in fibrous clays (in contrast to smectites) rheological properties remain constant even at high ionic strengths and over a wide pH range. Furthermore, montmorillonite does not adsorb negatively charged polymers, whereas sepiolite adsorbs them efficiently, enabling the preparation of negatively charged nanocomposites [15]. Illite and illite/smectite have proven to be effective platforms for the preparation of nanocomposite superadsorbents [17], but they should presumably behave like montmorillonite in terms of fluidity, clay/polymer ratio and binding of negatively charged polymers.

The effluent and coagulant charges were measured by means of a PCD (Mütek PCD 03) with an automatic titration unit (Mütek titrator T2) using charge-compensating polyelectrolytes as described by Rytwo et al. [18]. Results were normalized to $\text{mmol}_c \text{L}^{-1}$ of effluent or coagulant suspension, accordingly. TSS concentration was determined by filtering 1–5 mL of the sample through a 47-mm glass fiber membrane (Sartorius Stedim Biotech GmbH) with a pore diameter of 0.45 μm , and

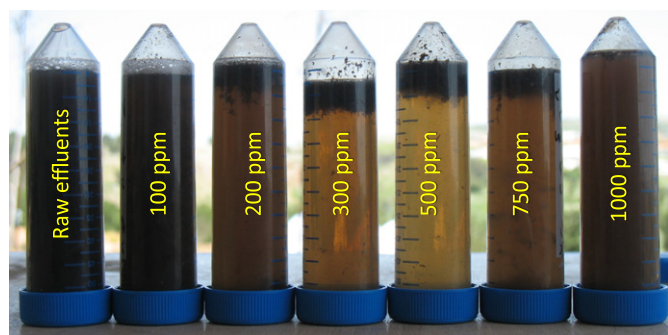


Fig. 1. Olive mill wastewater (OMW; initial charge of $-1900 \mu\text{mol L}^{-1}$) treated with the NC21Z doses indicated on the tubes.

drying at 105°C for 1 h. Turbidity was measured with a LaMotte 2020 turbidimeter. All experiments were performed in triplicate.

The results are shown in Table 1. Measuring the charge of the effluents and the charge of the coagulant suspension yields a straightforward evaluation of the volume of coagulant to be added to achieve efficient clarification. In this case, with an effluent charge of $-1900 \mu\text{mol}_c \text{L}^{-1}$ and a charge of $+89,000 \mu\text{mol}_c \text{L}^{-1}$ for the 2.5% NC21Z suspension, complete neutralization was expected from adding 21 mL of coagulant per L effluent (equivalent to 533 ppm NC21Z nanocomposite). Results in Table 1 show that indeed, a final NC21Z concentration of 500 ppm yielded 97% turbidity removal.

Fig. 1 illustrates the effect at 300 and 500 ppm added coagulant, the effluents are relatively clear and colloids have efficiently aggregated, forming a dense layer of flocs at the top of the tubes.

To confirm the feasibility of the suggested practice, another test was performed: highly charged raw OMW (initial charge of $-5400 \mu\text{mol}_c \text{L}^{-1}$) was treated with 5% suspensions of three different nanocomposite coagulants: (a) low charge (based on 800 mg chitosan per g clay), (b) medium charge (based on 500 mg PD per g clay), and (c) high charge (based on 2200 mg PD per g clay). Table 2 summarizes the charges and calculated doses needed to neutralize the effluent colloids.

A dispersion analyzer (LUMiSizer 6110) instrument was used to determine aggregation and clarification by recording the transmission of near-infrared light during centrifugation over the total length of a cell containing the suspension. The instrument determines the time-dependent position of the interface panicle-free fluid/suspension or sediment [19], and thus separation of the colloids from the suspension can be monitored in real time. This instrument could prove useful in evaluating the stability and sedimentation behavior of colloidal particles [20]. Wastewater-treatment experiments enable very rapid and accurate evaluation of the efficiency of colloid aggregation due to coagulant addition [15] as compared to the conventional “jar test” [21]. Profiles were taken every 5 s for 10 min at a relative centrifugal force (RCF) of $4.98 g$ (200 rpm). All experiments were performed three times.

Fig. 2 shows the average light transmission through the upper 90% of the test tube as a function of time, after 2 min of centrifugation. When the doses of added coagulant were close to the calculated required

Table 2

Charges and calculated doses of coagulant required to neutralize highly charged OMW ($-5200 \mu\text{mol}_c \text{L}^{-1}$).

	Charge (mmol L^{-1})	Required volume of coagulant (mL L^{-1})
Raw OMW	-5.2	
Low-charge coagulant	63.5	81.9
Medium-charge coagulant	124	41.6
High-charge coagulant	589	8.8

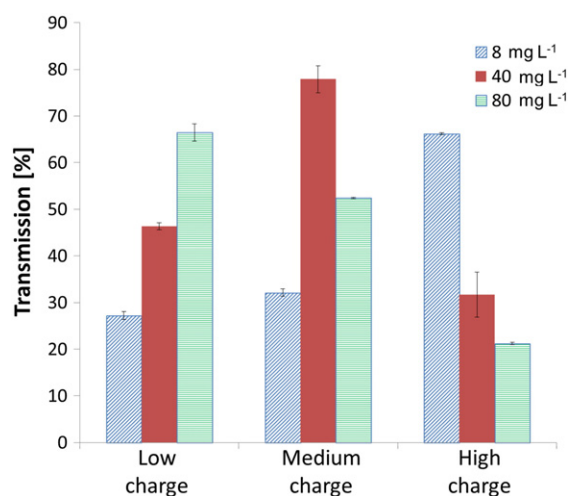


Fig. 2. Light transmission of olive mill wastewater after 2 min of centrifugation with different doses of low-, medium- or high-charge coagulants.

doses (8.8, 41.6 and 81.9 mL coagulant suspension L^{-1} effluent of low-, medium- or high-charge coagulant, respectively), light transmission of the effluent as measured by the dispersion analyzer was considerably higher than at the other doses, indicating efficient colloid aggregation and clarification of the effluent. Measurements at longer times showed decreased differences between treatments. However, even after 10 min of centrifugation, the optimal treatments were those in which the charges of the effluents and coagulants were equalized.

The presented effect is not unique to OMW effluents or nanocomposite-based coagulants. Fig. 3 shows the dispersion-analyzer measurements, after 30 and 150 s of centrifugation at 5 g RCF, of the clarification of cowshed wastewater with a charge of $-2480 \mu\text{mol}_c \text{L}^{-1}$ by means of three different coagulants: nanocomposite-based NC21Z ($+89,000 \mu\text{mol}_c \text{L}^{-1}$), a solution of 40% aluminum sulfate ($+108,000 \mu\text{mol}_c \text{L}^{-1}$) and a solution of 10% commercial PD ($+620,000 \mu\text{mol}_c \text{L}^{-1}$). Coagulants were added at doses equivalent to 25, 50, 100, 125 and 200% of those required to neutralize the colloids in the effluent. When the doses of added coagulant were close to neutralizing the effluents, higher light transmission was observed, reaching values close to those of water. At longer centrifugation times (150 s), clearer effluents were obtained, but the optimal value was reached near neutralization of the effluent colloids.

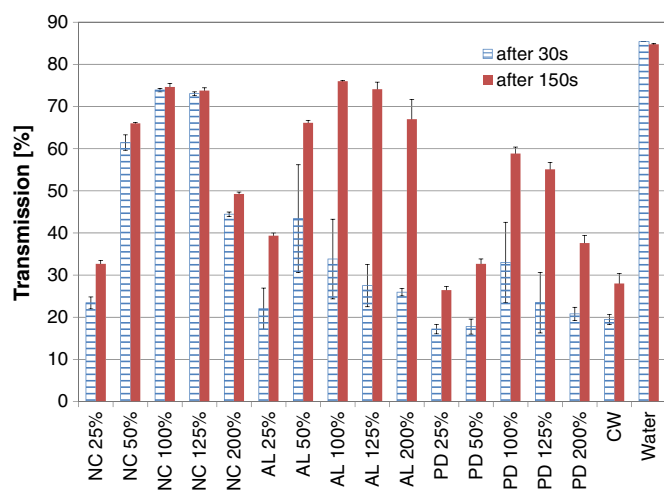


Fig. 3. Light transmission of cowshed effluents (CW, charge of $-2480 \mu\text{mol}_c \text{L}^{-1}$) treated with three different coagulant suspensions (nanocomposites – NC, aluminum sulfate – AL, commercial PD), at doses equivalent to 25, 50, 100, 125 and 200% of that required for effluent neutralization.

The proposed method for achieving efficient colloidal destabilization by measuring effluent and coagulant colloidal charges, followed by simple evaluation of the amount of coagulant needed to neutralize the effluent colloids, seems trivial. Nevertheless, no implementation of this method was found in the literature, presumably due to the fact that measuring charge with a PCD is less common than ζ -potential measurements. However, due to its simplicity, this procedure might be adopted by other researchers interested in destabilization of colloidal suspensions.

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