Comparison of selected methods for relative assessment of surface charge on waste sludge biomass

F Bux[1] and HC Kasan[2]*

[1]Department of Microbiology, University of Durban Westville, Private Bag X54001, Durban 4000, South Africa
[2]Department of Biotechnology, Technikon Natal, PO Box 953, Durban 4000, South Africa

Abstract

Industrial pollution has directed much concern about contamination of fresh-water systems by metal-laden effluents. Research has shown that activated sludge has potential for the removal of heavy metals from contaminated effluents. Much of the biosorptive capacity of the sludge may be attributable to the net negative charge present on the sludge surface, thus facilitating binding to positive metal cations. Detection of surface charge may serve as an excellent indicator of the adsorption potential of sludges and other potential biosorbents. Ten waste activated sludges were screened for surface charge using 3 different methods, viz., streaming current method, millivolt quantification method and the colloid titration technique. All 3 methods were capable of detecting surface charge and facilitated ranking of 10 sludges on the basis of electronegativity. Although charge determination using the titration method has most frequently been used, the millivolt quantification technique proved to be a more feasible and applicable method to detect surface charge of suspended sludge solids. The results from 3 methods employed showed that the sample from Southern Works, S9, was most electronegative.

Introduction

Activated sludge biomass is composed of eubacteria, filamentous bacteria, fungi, yeast, algae and protozoa (Jenkins et al., 1986; Bux et al.,1992; 1993). Several studies have shown that the activated sludge treatment process is capable of reducing metal-ion concentrations from waste-water (Brown et al., 1973; Chen et al., 1974; Lester et al., 1983; Fletcher and Beckett, 1987a). Many workers have attributed this finding to physico-chemical interactions between metal ions and sludge surfaces (Stoveland and Lester, 1980; Sterritt et al., 1981; Fletcher and Beckett, 1987b; Lake et al.,1989). Sludge surfaces are polymeric in nature comprising of protein, carbohydrate, nucleic acids and lipid (Goodwin and Forster, 1985). Sludge biomass is negatively charged due to the ionisation of inorganic groups such as carboxylic, aliphatic, aromatic, hydroxyl, sulphate and amino groups (Hughes and Poole, 1989).

Recent findings have conclusively shown that waste activated sludges from a variety of sources are capable of biosorbing several metal-ion species from solution (Swalaha and Kasan, 1992; Kasan, 1993). Since the biosorption of metal cations to sludges is dependent on the sludge surface charge, the objective of this study was to determine the relative charge on 10 waste activated sludges via comparison of 3 different methods, viz. streaming current, millivolt quantification and colloid titration techniques.

Materials and methods

Grab samples of return activated sludge were obtained from waste-water treatment plants in Natal, namely: Umlaas, S1; Amanzimtoti, S2; New Germany, S3; Hammarsdale, S4; Pietermaritzburg, S5; Kwa Mashu, S6; Tongaat, S7; Northern Works, S8; Southern Works, S9 and Phoenix, S10. Sludges were concentrated to 25 000

---

* To whom all correspondence should be addressed.

mg·ℓ^{-1} by centrifugation using a J6B Beckman centrifuge at 3 500 x g for 30 min and pellets were resuspended in 100 mℓ deionised water in sealed bottles and stored at 4°C for further use. The electronegativity of the sludge particles was determined within 48 h of obtaining samples utilising different methods, i.e. streaming current method, use of a pH/millivolt meter and modification of a colloid titration technique as described by Kawamura and Tanaka (1966).

Streaming current method

The movement of like charges is defined as an electrical current. This current is called the streaming current. The streaming current monitor utilises the principle of streaming current to obtain a measure of the colloidal charge and the values vary linearly with temperature. Streaming current is related to the zeta potential as follows (Smith and Somerset, 1971):

$$i \propto \frac{ZD}{N}$$

where:
  i = streaming current
  Z = zeta potential
  D = dielectric constant
  N = viscosity of fluid

Sludge samples S1 to S10 were diluted to a final volume of 100 mℓ and standard concentration of 5 000 mg·ℓ^{-1} using deionised water. The procedure involved using a Chemtrac Model 2 000 x R streaming current monitor (Floccotan, SA). The unit was initially flushed for approximately 15 min with distilled water and subsequently standardised with deionised water. A 50 mℓ syringe was used to inject sludge samples into the boat of the monitor. Results were recorded when constant negative streaming current values were acquired. This procedure was conducted in triplicate. The instrument was rinsed with deionised water between each of the samples tested.

Millivolt quantification method

A Beckman 50 combination pH/millivolt meter was used. The meter was standardised using standard buffer solutions of pH 7 (Beckman), since the solution has no net charge. Sludges 1 to 10 were diluted to final volume of 100 mℓ with deionised water in conical flasks at a concentration of 5 000 mg·ℓ^{-1}. The unit was operated at mV/Rel mV mode and tested with triple deionised water which produces no charge. Sludge samples were read in triplicate and the combination electrode rinsed with deionised water between each reading.

Modified colloid titration technique

Five mℓ of each of the sludge samples (S1 to S10) of 500 mg·ℓ^{-1} concentrations were pipetted into 50 mℓ conical flask in triplicate. Three drops of 0,1 % of toluidine blue (TB) indicator was added to each of the flasks. Contents of the flasks were mixed using a magnetic stirrer. An aliquot of 3,5 mℓ of standard positive colloid i.e. 0,001N methyl glycolchitosan (MGC) (Merck) was added and mixed for 10 s. This resulted in a blue colour. Excess positive colloid was then back - titrated with 0,01 N potassium polyvinyl alcohol sulphate (PVSK) (Aldrich) i.e. standard negative colloid, using a 10 mℓ burette. The pH of PVSK was adjusted to that of MGC with small additions of 0,1 M NaOH. The colour change from blue to purple indicated by the addition of 2 to 3 drops of PVSK was the end point. If purple colouration remained for 30 s to 2 min, then end point was stably reached. In addition to the flask containing the sludge sample, a deionised water (5 mℓ) blank was treated in the same manner, with the rest of the additions to the blank being the same.

The colloidal charge of the sample was determined by the following calculation (Kawamura and Tanaka, 1966):

Colloidal charge of
sample in milliequivalents = (sludge titration(mℓ) - blank
per litre   titration(mℓ)) x10^{-3}

but for sludge samples it is preferable to express charge per gram of dried sludge solids:

Charge of sample
in milliequivalents per = (sludge titration(mℓ) - blank
gram of suspended solids   titration(mℓ)) x2
               = m Eq/g suspended solids

Results and discussion

The significance of the different methods used during the present research was to compare the abilities of these techniques to assess surface charge and compare the results between 10 sludges rather than to determine the absolute charge on individual sludge surfaces. The colloid titration technique is the conventional and most widely used method to detect surface charge of colloids (Kawamura and Tanaka, 1966; Tiravanti et al., 1985; Morgan et al., 1990). During the present study, this method was modified for application to sludges. The streaming current method for charge detection is utilised primarily by the flocculant manufacturing industry. Neither the latter method nor the millivolt technique have been reported to be used for detection of surface charge on sludges.

The surface charge determined by using the streaming current monitor were referred to as streaming current values (Table 1) (Smith and Somerset, 1971). Some sludges were found to be less

TABLE 1 ELECTRONEGATIVITY OF 10 WASTE ACTIVATED SLUDGES USING THE STREAMING CURRENT METHOD		
Sludge	**SCV**	**%RSD**
1	-0,28	21,43
2	-0,36	5,56
3	-0,25	88,0
4	-0,17	29,41
5	-0,55	30,91
6	-0,42	11,90
7	-0,10	0,00
8	-0,22	18,18
9	-1,47	10,20
10	-0,43	0,00
SCV = streaming current value		

TABLE 2 ELECTRONEGATIVITY OF 10 WASTE ACTIVATED SLUDGES USING THE pH METHOD		
Sludge	**Millivolts**	**%RSD**
1	-54,63	0,82
2	-64,70	0,54
3	-61,50	0,60
4	-63,90	1,71
5	-35,16	0,88
6	-68,80	0,71
7	-33,40	1,77
8	-29,87	0,13
9	-79,27	0,15
10	-19,37	0,46

negative than others; S9 was most negative and S7 least negative. The use of a pH/millivolt meter which was adapted to millivolt mode to detect surface charge (Table 2) showed S9 as most negative with S10 being the least negative sludge. It is important to note that when using this method, although conductivity is detected, it is reflective of the charge in the solution which is dictated by the charge on the sludge surface, since the suspension medium i.e. distilled water has no conductivity or net charge present. Therefore the pH meter on millivolt mode could be used to detect differences in surface charge among sludges. The findings of the latter method partially substantiated the results of the conventional method of charge detection on sludge surface, i.e., colloid titration technique (Kawamura and Tanaka, 1966). The calculated surface charges of the sludges as shown in Table 3 are expressed as milliequivalents per gram of suspended solids. Interestingly, S9 again proved to be the most negatively charged sludge.

When comparing the 3 methods there was relative similarity in ranking of the high order sludges, viz. S9 and S6, whilst the middle and lower order sludges did not follow a similar pattern, displaying noticeable variations (Table 4). There was substantial difference in the magnitude of electronegativity of the high order sludge, i.e.

TABLE 3
ELECTRONEGATIVITY OF 10 WASTE ACTIVATED SLUDGES USING THE TITRATION TECHNIQUE

Sludge	PVSK	mEq/g SS (ml)	%RSD
1	10,56	-15,24	4,46194
2	08,80	-18,76	1,17271
3	09,18	-18,00	0,55556
4	09,67	-17,02	0,99882
5	11,92	-12,52	1,4377
6	07,19	-21,98	0,59145
7	11,34	-13,68	3,07018
8	07,26	-21,84	0,27473
9	03,25	-29,86	0,56932
10	10,61	-15,13	2,01586
B	18,18		

B = Blank

TABLE 4
RANKING OF 10 WASTE ACTIVATED SLUDGES ACCORDING TO THEIR ELECTRONEGATIVITIES USING 3 DIFFERENT METHODS

Ranking	Streaming current method	pH meter	Titration
1	9	9	9
2	5	6	6
3	10	2	8
4	6	4	2
5	2	3	3
6	1	1	4
7	3	5	1
8	8	7	10
9	4	8	7
10	7	10	5

one of the main components contributing to the overall negative value of the zeta potential of activated sludge surfaces. Research conducted by Horan and Eccles (1986) showed that the nature and concentration of the ionogenic materials present at sludge surfaces will determine the magnitude of the sludge surface charge. Morgan et al. (1990) demonstrated that using the colloid titration technique, the surface charge for sludge solids from 9 sources ranged from -0,110 to -0,907 m Eq/g SS. In contrast to these findings, the results of the present study showed that using the same charge detection method, the charges on the sludges under investigation ranged from -12,52 to -29.86 m Eq/g SS, thus displaying much greater electronegativity. This high degree of sludge electronegativity could be attributable to the nature of the individual sludge surfaces.

Overall, comparison of results showed that the titration and pH meter methods produced similar ranking patterns, indicating that these techniques share similar limits of detection. In addition, assessment of accuracy among the different methods used present the pH meter method to be superior, followed by the titration method due to minimal fluctuations in the percentage relative standard deviation (RSD) (Tables 1 to 3). There are several other benefits associated with the use of the pH meter method, compared with the modified titration method viz., the technique is less time-consuming, it facilitates on-site field testing, it can be more accurate and precise due to its simplicity and the absence of the need for colour indication. In conclusion, both the titration and pH meter methods appear to be suitable to compare surface charge among sludges, although the latter method is more appropriate. Present research investigates the relationship between the superior electronegativity of S9, determined during the present study, and its capacity to biosorb a variety of metal ions from solution compared to the 9 other sludges.

Acknowledgements

S9 and the rest of the sludges (Tables 1 to 3). This large difference in surface charge was detected by all three methods employed. The magnitude of difference in charges between the middle and lower order ranked sludges was small (Tables 1 to 3). Therefore, the sensitivities of each of the techniques employed for charge detection influenced the ranking of these sludges. The 3 methods utilised to determine electronegativity of sludge biomass showed that all sludges tested produced an overall net negative charge. Several hypotheses have been suggested to explain this complex phenomenon (Forster, 1976) e.g., the chemical nature of the sludge surface influences the magnitude of the surface charge which subsequently affects the settlement properties of the sludge. The principle ionogenic component of sludge polysaccharide was shown to be glucuronic acid which, at neutral pH, contributes a strong negative charge, thus facilitating the polysaccharides to behave as a polyelectrolyte (Stumm and Morgan, 1962; Forster, 1971). Brown and Lester (1979) concluded that hexuronic acid is

References

BROWN, HG, HENSLEY, CP, MC KINNEY, GL and ROBINSON, JL (1973) Efficiency of heavy metals removal in municipal sewage treatment plants. *Environ. Lett.* 5 103-114.

BROWN, MJ and LESTER, JN (1979) Metal removal in activated sludge: The role of bacterial extracellular polymers. *Water Res.* 13 817-837.

BUX, F, ISHWARLALL, AD and KASAN, HC (1992) Diversity of bacterial communities in activated sludge plants in Natal. *Proc. 6th Int. Symp. Microbial Ecol.* 129.

BUX, F, ISHWARLALL, AD and KASAN, HC (1993) A microbiological survey of ten activated sludge plants. *Water SA* 20 (1) (In press).

CHEN, KY, YOUNG, CS and ROHATGI, N (1974) Trace metals in waste-water effluents. J. *Water Pollut. Control Fed.* 46 2663-2675.

FLETCHER, P and BECKETT, PHT (1987a) The chemistry of heavy metals in digested sewage sludge -1. Copper (II) complexation with soluble organic matter. *Water Res.* 21 1153-1161.

FLETCHER, P and BECKETT, PHT (1987b) The chemistry of heavy metals in digested sewage sludge - II. Heavy metal complexation with soluble organic matter. *Water Res.* 21 1163-1172.

FORSTER, CF (1971) Activated sludge surfaces in relation to the sludge volume index. *Water Res.* **5** 861-870.

FORSTER, CF (1976) Bioflocculation in the activated sludge process. *Water SA* **2** 119-125.

GOODWIN, JAS and FORSTER, CF (1985) A further examination into the composition of activated sludge surfaces in relation to their settlement characteristics. *Water Res.* **19** 527-533.

HORAN, NJ and ECCLES, CR (1986) Purification and characterization of extracellular polysaccharide from activated sludge. *Water Res.* **20** 1427-1528.

HUGHES, MN and POOLE, RK (1989) *Metals and Micro-organisms.* Chapman and Hall, London, New York. 10 pp.

JENKINS, D, RICHARD, MG and DAIGGER, GT (1986) Manual on the Causes and Control of Activated Sludge Bulking and Foaming. Water Research Commission, Pretoria.

KASAN, HC (1993) The role of waste activated sludge and bacteria in metal-ion removal from solution. *Crit. Rev. Environ. Sci. Tech.* **23** 79-117.

KAWAMURA, S and TANAKA, Y (1966) The application of colloid titration techniques to coagulant dosage control. *Water Sewage Works* **133** 348-357.

LAKE, DC, KIRK, PWW and LESTER, JN (1989) Heavy metal solid association in sewage sludges. *Water Res.* **23** 285-291.

LESTER, JN, STERRITT, RM and KIRK, PWW (1983) Significance and behaviour of heavy metals in waste water treatment processes. *Sci. Total Environ.* **30** 45-83.

MORGAN, JW, FORSTER, CF and EVISON, L (1990) A comparative study of the nature of biopolymers extracted from anaerobic and activated sludges. *Water Res.* **24** 743-750.

SMITH, CV and SOMERSET, IJ (1971) Streaming Current Technique for Optimum Coagulant Dose. Civil Engineering Department. Univ. of New York.

STERRITT, RM, BROWN, MJ and LESTER, JN (1981) Metal removal by adsorption and precipitation in the activated sludge process. *Environ. Pollut.* **24** 313-323.

STOVELAND, S and LESTER, JN (1980) A study of the factors which influence metal removal in the activated sludge process. *Sci. Total Environ.* **16** 37-54.

STUMM, W and MORGAN, JJ (1962) Chemical aspects of coagulation. *J. Amer. Water Works Assoc.* **54** 971.

SWALAHA, FM and KASAN, HC (1992) Potential application of waste sludges. *Proc. 18th Water, Environ. Management Conf.* **1** 260-262.

TIRAVANTI, G, LORE, F and SONNANTE, G (1985) Influence of the charge density of cationic polyelectrolytes on sludge conditioning. *Water Res.* **19** 93-97.