



Investigation of Electrokinetic Properties of Natural Vine Stem Dispersions as Biosorbent

EBRU MAVIOGLU AYAN, ESRA EVRIM YALÇINKAYA* and ASLI TOPTAS

Department of Chemistry, Science Faculty, Ege University, 35100 Izmir, Turkey

*Corresponding author: E-mail: esra.evrimsaka@ege.edu.tr

Received: 5 October 2013;

Accepted: 21 March 2014;

Published online: 1 September 2014;

AJC-15843

Vine stem is used as a low cost adsorbent for the removal of toxic dyes from the aqueous solutions. In this study, the effects of electrolyte concentration, pH and type of ionic species on the zeta potential of the natural vine stem dispersions were investigated by microelectrophoresis method. ζ -Potential experiments have been performed to determine the point of zero charge (pzc) and potential determining ions (pdi). The surface charge of vine stem exhibited an increasing negativity as the pH of the solution increased. Vine stem dispersions do not have point of zero charge. A gradual decrease in the ζ -potential occurs with the monovalent electrolytes when concentration increased. Divalent and heavy metal electrolytes have less negative potentials due to the higher valence of ions. The ζ -potential values have had a positive sign at trivalent electrolytes.

Keywords: Zeta potential, Natural vine stem, Electrolytes.

INTRODUCTION

The adsorption methods removed the toxic materials do not leave behind any toxic degraded products or disturb the quality of water. Different materials especially lignocellulosic wastes have been used as adsorbents¹⁻³. The vine stem was used as low cost adsorbent for the removal of acidic and basic dyes from the aqueous solutions. The adsorption properties of vine stem with the acidic and basic dyes have been investigated in our previous study⁴. The utilization of vine stem and similar plant residues for waste water treatment is advantageous because their polyol structures adsorb various toxic materials well. Also they are low-cost and available abundantly. There are many studies on the use of low-cost materials for adsorption, such as jackfruit peel⁵, coal⁶, lignite⁷, chitosan⁸, fly ash⁹, kaolinite¹⁰, montmorillonite¹¹, zeolite¹², organo-attapulgite¹³, rice husk ash¹⁴ and oreganum stalks¹⁵ contribute significantly to the adsorption mechanism.

The electrokinetic properties contribute significantly to explanation of the adsorption mechanism of various species (organic and inorganic) at the solid-solution interface. In the suspension systems, they control coagulation, flotation, dispersion properties, give important information about the electrical properties and the interactions with surrounding medium of particles¹⁶. So, the influence of the particle charge on the filtration, flow, sedimentation and aggregation behaviour can be estimated¹⁷. Electroosmosis and streaming potential^{18,19} and particularly electrophoresis^{20,21} are among the most frequently

used techniques to determine the electrokinetic properties of particles. The measurement of the electrophoretic mobility of the colloidal particles in suspension that is usually characterized by the ζ -potential which is a key technique for the determination of the surface properties of the particles. Suspended particles will migrate at mobility proportional to their surface charge in an electric field. The applied electric field convicts the charged fluid in the double layer around the particle, causing electrophoretic migration in the opposite direction. Since the combination is electrically neutral, there is no net force on the particle and its double layer. The result is an electric double-layer and an electric potential across the layer called zeta potential^{22,23}. For many applications, the sign and the magnitude of the ζ -potential must be known. In a heterogeneous suspension, particles with different surface charges will have different electrophoretic mobility, leading to the possibility that they will colloid and aggregate. The electrolytes can have a significant impact on the ζ -potential. The effect depends on the relative valence of the ions and on their concentration²⁴.

When vine stem is incorporated into the aqueous dispersions, surface interactions occur at the interface. The variation of the ζ -potential and the electrical double layer properties of the surface as a function of electrolyte type, concentration and pH in vine stem have not been yet determined. The purpose of the study is to investigate various effects such as pH, type of ionic species and a wide range of electrolyte concentration on the ζ -potential of the natural vine stem dispersions.

EXPERIMENTAL

The vine stem was supplied from a vineyard in the Manisa/Turkey area. The samples were washed with bidistilled water to remove the surface-adhered particles and water soluble materials. They were air-dried for several days, ground and sieved to particle < 0.2 mm. The properties of this material are given in Table-1. The adsorbent was characterized as explained in our previous study¹⁵.

The electrophoresis method was used to determine the ζ -potential of the adsorbent, by using Zeta-Meter 3.0+ (with Zeiss DR microscope, GT-2 type quartz cell, molybdenum cylinder anode and platinum rod cathode electrode). All chemicals were A.R. grade and supplied from Merck.

ζ -Potential measurements: When two phases are placed in contact, there generally occurs a difference in potential between them. The ζ -potential is an indicator of the surface charge properties of a colloid or a particle in solution and varies depending on the surface potential and the thickness of the electric double layer. It has been determined by using electrophoresis method in this study. The ζ -potential of the vine stem dispersions was calculated automatically from measured electrophoretic mobilities employing the Smoluchowski Equation²⁵.

$$\mu = \frac{\epsilon_r \epsilon_0 \zeta}{\eta} \quad (1)$$

In this equation; ζ : zeta potential; η : viscosity of the medium; μ : electrophoretic mobility at the actual temperature; ϵ_r : the dielectric constants of the medium; ϵ_0 : the dielectric constants of free space. The pH (range: 2-10) of the dispersions were adjusted by HCl or NaOH solutions and measured with WTW pH meter (electrode: combine glass electrode). The ζ -potentials of these samples were measured as a function of pH without addition of electrolytes.

0.5 g/L of dry adsorbent was added to the aqueous solutions of mono- (NaCl, KCl, LiCl, RbCl, CsCl, NaNO₃, NaCH₃COO), di- (CaCl₂, MgCl₂, BaCl₂, SrCl₂, Na₂CO₃, Na₂SO₄) and trivalent (AlCl₃, FeCl₃, CrCl₃) ions and divalent metal salts such as ZnCl₂, CuCl₂, NiCl₂, CoCl₂, MnCl₂, CdCl₂ and Pb(NO₃)₂ in a 10⁻¹-10⁻⁵ M concentration range. The electrophoresis cell was carefully washed with deionized water and always conditioned with the test suspension before each measurement to prevent cross contamination. Three parallel measurements were conducted and the averages were reported. All solutions were prepared by using distilled deionized water (< 2.0 μ S/cm). Each of the dispersions were shaken in a thermostatic shaker at 25 °C for 2 h at a constant pH to establish equilibrium. The applied voltage during the measurements was varied in the range 50-150 mV.

RESULTS AND DISCUSSION

The amount of solid particles governed the generation of surface charge by producing the ionic species at the solid/liquid interface and then affected the ζ -potential value of the suspension. So, the variation of the ζ -potential versus the solid concentrations of vine stem was determined. It was found that the ζ -potential values were not affected by the vine stem amount and remained stable in the concentration range 0.50-1 g/L. Therefore, in the subsequent ζ -potential measurements, the clay to liquid ratio was kept constant at 0.5 g/L. On the other hand, the ζ -potential measurement was not also influenced by the shaking time. The optimum shaking time was determined to be 2 h.

pH Effect: Change in ζ -potential with pH for colloidal dispersions of vine stem particles is reflected in Fig. 1. It can be concluded that natural vine stem surface is negatively charged within the whole range of pH having no isoelectric point (IEP) The ζ -potential negativity of the adsorbents was increased with the increasing the pH of the solution slightly from 2 to 10. This increase may be due to the adsorption of OH⁻ ions onto the positive charge centers of vine stem particles or the deprotonation of surface hydroxyl groups and the reaction between the OH⁻ and the dissolved cations to form metal hydroxides. Also, the H⁺ adsorption could be occurred on the negative charge centers at low pH. A similar trend was observed both in the oreganum stalks which were a kind of lignocellulosic waste and the biomass *R. fraxinea*^{15,26}.

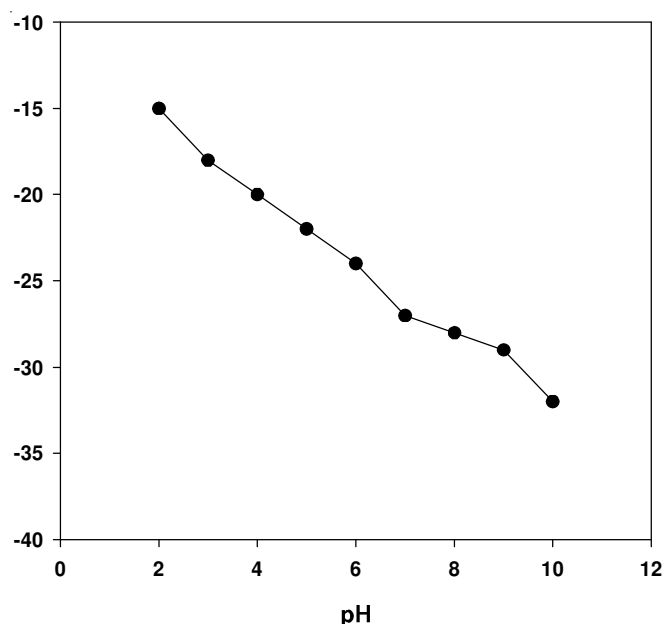


Fig. 1. Zeta potential of the vine stem as a function of pH

TABLE-1
PROPERTIES OF VINE STEM

Proximate analysis, wt. % (as received)	Main constituents, wt. % (on dry basis)	Amounts of oxygen-containing functional groups (mmol g ⁻¹)			
Moisture	12.1	Lignin	20.3	Total acidic groups	n.d
Ash	6.5	Hemicellulose	36.4	Total basic groups	1.16
		Cellulose	38.7		
		Extractives	4.6		

Electrolyte concentration effect: Fig. 2a (for monovalent cations, *i.e.* LiCl, NaCl, KCl, RbCl and CsCl) and Fig. 2b (for monovalent anions *i.e.* NaCl, NaNO₃, CH₃COONa) show comparison of the effect of monovalent electrolyte concentration on electrokinetic properties of the vine stem particles (pH: 5.3 ± 0.2). As seen in Fig. 2, the ζ-potential is negative for monovalent cations and anions in accordance with some previous studies^{25,27}. For monovalent anions, the negative ζ-potential decreased in order that Cl⁻ > CH₃COO⁻ > NO₃⁻. Cl⁻ anions is smaller than that of CH₃COO⁻ and NO₃⁻, which means that of Cl⁻ can easily enter to Stern layer and increase the negative ζ-potential values.

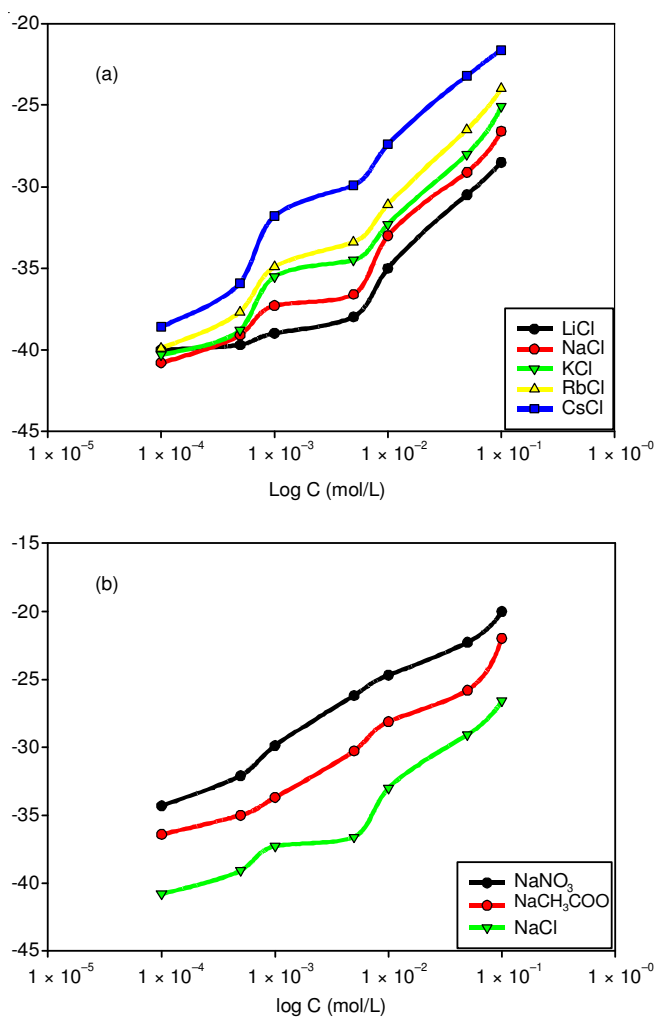


Fig. 2. Zeta potential of the vine stem particles as a function of monovalent electrolyte concentration; (a) cations and (b) anions

The ζ-potential of natural vine stem particles decreased with an increasing electrolyte concentration from 10⁻⁵ to 10⁻¹ M due to compression of the double layer (eqn. 2). Monovalent cation adsorbs in the electrical double layer as a counter ion with coulombic attractions on negatively charged particle surface and compress the thickness of the electrical double layer; and results with less negatively charged surface and cause reduction in ζ-potential. This result could be explained by the relationship between ionic strength and thickness of the electrical double layer with the equation:

$$\frac{1}{\kappa} = \frac{3}{ZC^{1/2}} \quad (2)$$

where; 1/κ: thickness of the diffuse layer (Å); Z: valency; C: ion concentration (mol/L). This equation indicates that for the same cation concentration, the valency of ion contributed significantly to the thickness of double layer and consequently caused a change of the ζ-potential. So, the thickness of the electrical double layer decreases with increasing concentration. Thus, ζ-potential values of the particles reduces. It was observed that the size of the hydration ion affects both the thickness of the Stern layer and also the ζ-potential. The particles with smaller hydration radius could migrate preferentially to the particle surface. So, they could enter the Stern layer easily and the ζ-potential became more positive. For all the monovalent cations, the ζ-potential increased in order that of Li⁺ > Na⁺ > K⁺ > Rb⁺ > Cs⁺ at any concentration. The more strongly hydrated the monovalent cations (Li⁺, Na⁺) are bound to the particle surface more weakly. Consequently they lead to more negative ζ-potential values²⁸. The less strongly hydrated monovalent cations like Rb⁺, Cs⁺, give rise to relatively low-zeta potentials.

Fig. 3a and 3b presents the changing of the ζ-potential of the particles with electrolyte concentrations in the presence of divalent electrolytes. With the addition of divalent electrolytes into the dispersion medium, the surfaces of particles become more positively charged due to the adsorption of divalent ions and shift the ζ-potential of dispersion more positive values. Divalent anions (*i.e.* CO₃²⁻ and SO₄²⁻) were not potential determining ion for vine stem particles, but it decreased the thickness of the electrical double layer and contributed instability of the colloidal system similar to chloride anion. Similarly of divalent ions, the ζ-potential values were zero at high concentration of heavy metal ions (Fig 4). The particle charge was zero at concentrations higher than 10⁻¹ M due to the adsorption on the surface. The hydrated ion radius of divalent heavy metal ions and alkali earth ions are very similar to each other²⁹. Also, as the concentration of heavy metal ions increases, the dispersion pH of the vine stem decreases from 5 to 2.7. Reactions (1) and (2) (S: Solid and M: Metal) explained this decrease³⁰.

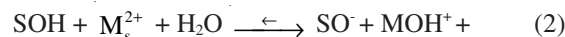
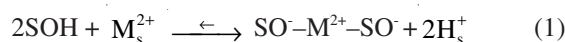


Fig. 5 shows the plots of the ζ-potential of vine stem as a function of trivalent electrolyte concentration. When the concentration increased from 1 × 10⁻⁵ to 1 × 10⁻¹ M, the ζ-potential values became more positive. A sharp increase occurred at 1 × 10⁻³ M for CrCl₃ and above this concentration, a charge reversal occurred and the ζ-potential values became positive. Because of the specific adsorption of Al³⁺, Fe³⁺ and Cr³⁺ counterions in the Stern layer, the charge of the particles were positive³¹. These ions can be called as potential determining ions. In the concentration range 1 × 10⁻⁵-1 × 10⁻¹ M, Al³⁺, Fe³⁺ and Cr³⁺ ions are in the non-hydroxyl form, electrolytes containing Al³⁺ undergo solvation, hydrolysis and polymerization reactions when they are dissolved in aqueous medium³². They can form hydroxyl complexes either at concentrations lower than 5 × 10⁻⁵ M or with increasing pH.

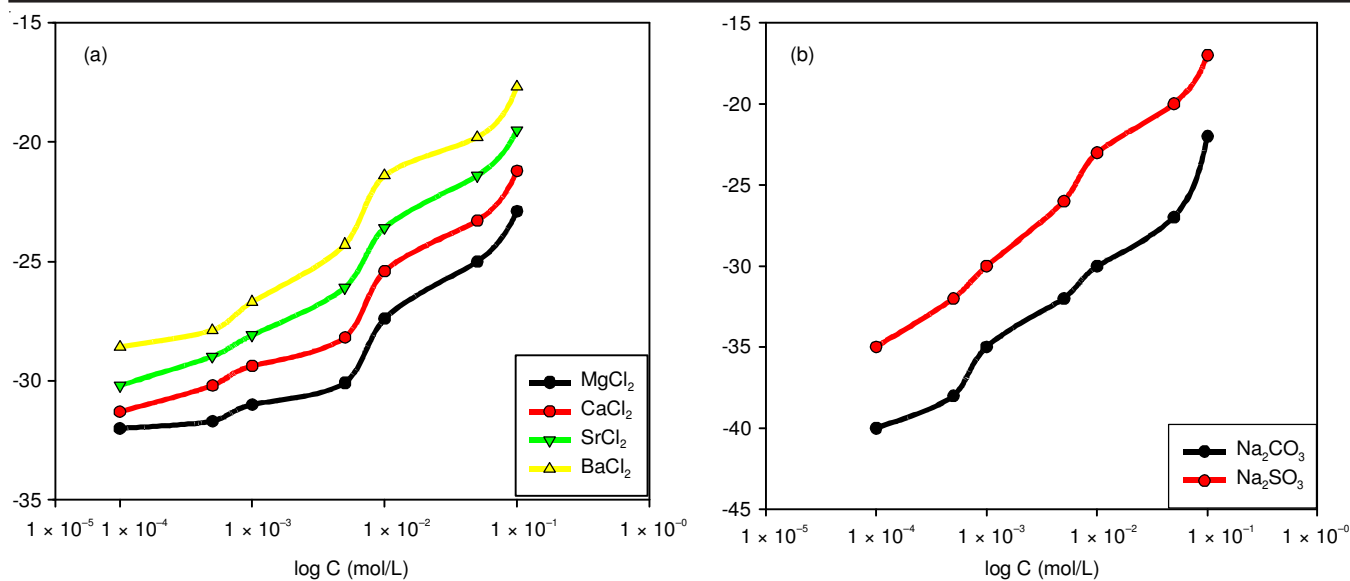


Fig. 3. Zeta potential of the vine stem as a function of divalent electrolyte concentration; (a) cations and (b) anions

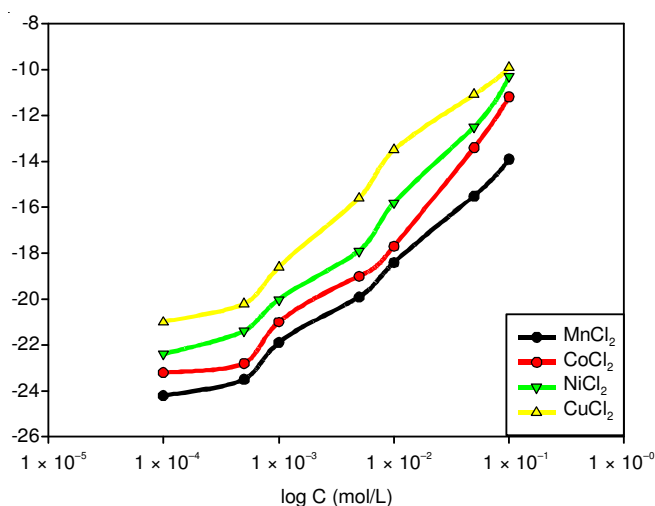


Fig. 4. Zeta potential of the vine stem as a function of heavy metal concentration

It can be clearly seen in the Fig. 5 that $AlCl_3$ reversed the surface charge of particle from negative to positive. The ζ -potential values were increased with the electrolytes in the order $Al^{3+} > Cr^{3+} > Fe^{3+}$. Namely, the dispersion which include the $AlCl_3$ electrolyte has the most positive ζ -potential value due to the small ionic radius. This ions could approach to surface closest in comparison with other trivalent ions.

Although all ions tended to reduce the ζ -potential, the trivalent ions were the most effective to reduce the ζ -potential, in accordance with the Schultz and Hardy rule³³. In the literature, atomic force microscopy experiments revealed that trivalent cations adsorb much more strongly on surfaces than mono- or di-valent ones^{24,25,34}. In present case, for all the $AlCl_3$ concentrations examined, charge reversal was occurred just for vine stem aqueous dispersions, besides; the dispersed particles dominantly caused by the specific adsorption of hydrolyzed Al ion species. Consequently, trivalent counter ions caused higher ζ -potential values of dispersion than monovalent and divalent ions.

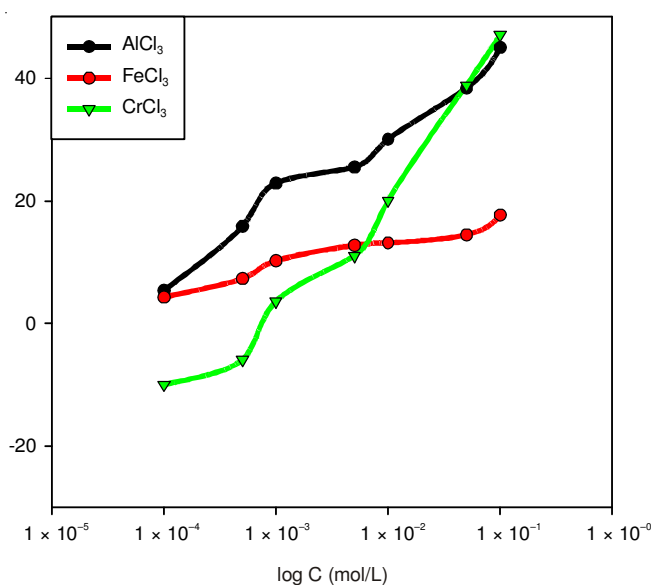


Fig. 5. Zeta potential of the vine stem as a function of trivalent electrolyte concentration

Conclusion

In this study, the ζ -potential of natural vine stem dispersions was determined by microelectrophoresis method. Natural vine stem is used as low cost adsorbent for the removal of toxic dyes from the aqueous solutions with high adsorption capacities. The effects of electrolyte concentration, pH and type of ionic species on the electrokinetic properties of the natural vine stem dispersions were investigated.

The dispersions of vine stem exhibit negative ζ -potential value in the pH range from 2 to 10. Vine stem dispersions have no isoelectrical point in the studied pH ranges.

The ζ -potential of vine stem particles in the presence of monovalent electrolytes *i.e.* LiCl, NaCl, KCl, RbCl and CsCl were shifted to less negative values with increasing electrolyte concentration from 10^{-5} to 10^{-1} M due to the compression of the double layer. Monovalent cations like Li^+ , Na^+ , K^+ , Rb^+

and Cs⁺ and anions like Cl⁻, NO₃⁻ and CH₃COO⁻ are identical electrolytes for vine stem dispersions. The ζ-potential of vine stem particles become more positive with increasing divalent cation and heavy metal concentration. For trivalent ions, the ζ-potential values become positive at high electrolyte concentrations because of adsorption of Al³⁺, Fe³⁺ and Cr³⁺ counter ions in the Stern layer.

The similar electrokinetic properties results were obtained with clay minerals that were studied in our previous studies. So this natural vine stem could be used alternate adsorbent to the usual clay minerals at considerably lower costs and higher adsorption capacities.

ACKNOWLEDGEMENTS

The authors thank Ege University Research Fund for financial supports.

REFERENCES

- B.C. Qi and C. Aldrich, *Bioresour. Technol.*, **99**, 5595 (2008).
- G. Annadurai, R. Juang and D. Lee, *J. Hazard. Mater. B*, **92**, 263 (2002).
- B.H. Hameed, *J. Hazard. Mater.*, **161**, 753 (2009).
- E.M. Ayan, A. Toptas, G. Kibrislioglu, E.E.S. Yalcinkaya and J. Yanik, *Clean-Soil, Air, Water*, **39**, 406 (2011).
- B.H. Hameed, *J. Hazard. Mater.*, **162**, 344 (2009).
- A.K. Mittal and C. Venkobachar, *J. Environ. Eng.*, **119**, 366 (1993).
- S.J. Allen, G. McKay and K.Y.H. Khader, *J. Chem. Technol. Biotechnol.*, **45**, 291 (1989).
- Y.C. Wong, Y.S. Szeto, W.H. Cheung and G. McKay, *Process Biochem.*, **39**, 695 (2004).
- D. Mohan, K.P. Singh, G. Singh and K. Kumar, *Ind. Eng. Chem. Res.*, **41**, 3688 (2002).
- L. Israel, C. Guler, H. Yilmaz and S. Guler, *J. Colloid Interf. Sci.*, **238**, 80 (2001).
- A.H. Gemeay, A.S. El-Sherbiny and A.B. Zaki, *J. Colloid Interf. Sci.*, **245**, 116 (2002).
- V. Meshko, L. Markovska, M. Mincheva and A.E. Rodrigues, *Water Res.*, **35**, 3357 (2001).
- H. Chen and J. Zhao, *Adsorption*, **15**, 381 (2009).
- S. Chandrasekhar and P.N. Pramada, *Adsorption*, **12**, 27 (2006).
- E. Mavioglu Ayan, P. Secim, S. Karakaya and J. Yanik, *Clean-Soil, Air, Water*, **40**, 856 (2012).
- P. Somasundaran and D.W. Fuerstenau, *J. Phys. Chem.*, **70**, 90 (1966).
- R.J. Hunter, *Zeta potential in Colloid Science*, Academic Press, London (1981).
- R.C. Srivastava and P.K. Avasthi, *J. Hydrol.*, **20**, 37 (1973).
- S.L. Swartzen-Allen and E. Matijevic, *J. Colloid Interf. Sci.*, **50**, 143 (1975).
- R.J. Hunter, *Zeta Potential in Colloid Science-Principle and Applications*, Academic Press, New York (1988).
- S. Rossi, P.F. Luckham and Th.F. Tadros, *Colloids Surf.*, **201**, 85 (2002).
- W. Pitsch, *Size Enlargement by Agglomeration*, Wiley, New York (1991).
- D.J. Shaw, *Colloid and Surface Chemistry*, Butterworth-Heinemann Ltd., Oxford, Great Britain (2010).
- M. Alkan, O. Demirbas and M. Dogan, *J. Colloid Interf. Sci.*, **281**, 240 (2005).
- E.E. Saka and C. Guler, *Clay Miner.*, **41**, 853 (2006).
- T. Tay, M. Candan, M. Erdem, Y. Çimen and H. Türk, *Clean-Soil, Air, Water*, **37**, 249 (2009).
- A. Delgado, F. Gonzalez-Caballero and J.M. Bruque, *J. Colloid Interf. Sci.*, **113**, 203 (1986).
- Y. Horikawa, R.S. Murray and J.P. Quirk, *Colloids Surf.*, **32**, 181 (1988).
- G. Zundel, *Hydration and Intermolecular Interaction*, Academic Press, New York (1969).
- R.O. James, J.A. Davis and J.O. Leckie, *J. Colloid Interface Sci.*, **65**, 331 (1978).
- R.M. Pashley and J.P. Quirk, *Colloids Surf.*, **9**, 1 (1984).
- A.C. Pierre and K. Ma, *J. Eur. Ceram. Soc.*, **19**, 1615 (1999).
- H. Van Olphen, *An Introduction to Clay Colloid Chemistry*, Chap. 7. Wiley, New York (1977).
- E.E. Yalcinkaya and C. Guler, *Sep. Sci. Technol.*, **45**, 635 (2010).