Influence of Temperature and Ion Concentration on Sedimentation Characteristics of Tricalcium phosphate (TCP) and Tristrontium phosphate (TSP) Precipitates

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ABSTRACT: Physical and chemical variables of insoluble salts generally affect sedimentation characteristics of precipitates. In this research study, the effects of temperature and ion concentration on the sedimentation of tricalcium phosphate (TCP) and tristrontium phosphate (TSP) were studied. The focus was to determine the sedimentation kinetics such as rate, order and rate constant of TCP and TSP at varying temperatures using the modified initial rate (Isolation) method. It was observed that whereas effect of temperature was not significant, low concentrations ($< 0.04M$) of the metal and phosphate ions markedly influenced the initial sedimentation rates of TCP and TSP precipitates. TCP sedimentation order ranged between 0.63 and 1.23 at constant phosphate ions concentration and between 1.52 and 2.10 at constant calcium ions concentration. TSP sedimentation order also ranged between 0.58 and 1.31 at constant phosphate ions concentration and between 1.55 and 1.81 at constant strontium ions concentration. Furthermore, ranges of sedimentation rate constants were obtained. At constant phosphate ions concentration, 1.80×10^{-4} - 1.57×10^{-3} and 1.51×10^{-4} - 2.45×10^{-3} were obtained for TCP and TSP, respectively. At constant metal ions concentration 1.71×10^{-5} - 9.54×10^{-5} and 5.70×10^{-5} - 1.12×10^{-4} were respectively obtained for TCP and TSP. Data may be employed as additional design information for modeling physiochemical phosphate removal in water treatment technology.

Sedimentation describes the motion of particles in suspension or molecules in solution in response to an external force such as gravity (Fatimi *et al.*, 2010). It is a physical process commonly used to remove impurities that have been rendered settleable by precipitation or flocculation in wastewater treatment technology. Rate data of sedimentation is useful in the design of sedimentation tanks and in modeling two-phase flow operations (Obunwo and Iboroma, 2015).

Mathematical models such as those by Stokes and Vesilind respectively describe sedimentation of particles in dilute and concentrated suspension media (Nutan and Reddy, 2010; Zhang *et al.*, 2015). According to Kazadi-Mbamba *et al.*, (2015) existing models have limited description for physico-chemical processes such as precipitation, possibly due to design limitations. However, Obunwo *et al*., (2017) postulated that they describe sedimentation data that originate purely from physical processes.

Suspensions prepared by precipitation methods (Patel, 2010) settle out in response to gravitational force and at different rates depending on concentration of the solutions before mixing and the degree of particle supersaturation in mixture after mixing. Precipitation conditions (Kirboga and Oner, 2013) that influence particle size and structure - temperature, concentration of reactants, stirring, pH of medium - also affect the sedimentation behaviour of resulting precipitates.

In continuation of our studies on sedimentation, we have investigated the effects of temperature and ion concentration on sedimentation properties of tricalcium and tristrontium phosphates in mother solution, by the modified Initial Rate (or Isolation) Method. The objective of this paper is to present the influence of temperature and ion concentration on sedimentation characteristics of tricalcium phosphate (TCP) and tristrontium phosphate (TSP) Precipitates.

MATERIALS AND METHODS
Materials such as analytical grade (BDH chemicals) trisodium phosphate, calcium chloride and strontium chloride hexahydrate were procured. Other materials employed included digital stopwatch, thermometer, Nuohai thermostated water-bath (Model Number XMTD-204) and a digital camera. A bench-scale settling apparatus (settleometer) was set up using 100ml measuring cylinder, a transparent measuring tape and stirring rod.

Treatment: Standard solutions (0.02M - 10M) of calcium chloride, strontium chloride and trisodium phosphate were prepared using de-ionised water. The experimental study approach employed for this study was the 'Modified Initial Rate or Isolation Method' (Atkins and Paula, 2006; Obunwo *et al.*, 2014).

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Known volumes (40mls) of varying concentration of either Ca^{2+} or Sr^{2+} (0.02M to 0.10M) and constant concentration of PO_4^{3-} (0.06M) were mixed directly to form either tricalcium phosphate (TCP), $Ca_3(PO_4)_2$, or tristrontium phosphate (TSP), $Sr_3(PO_4)_2$, precipitates. The precipitate suspension formed after mixing was stirred immediately for 30 seconds and then allowed to stand. The displacement of the suspension front (h) was monitored and recorded every 30 seconds, for 150 seconds. The procedure was reversed by varying the concentration of the PO_4^{3-} while keeping either Ca^{2+} or Sr^{2+} concentration constant. The experiments were performed in a thermostated water-bath set initially at 30^oC and were repeated at 35, 40, 45, 50, and 55^oC. A 3.1 watts LED rechargeable desk lamp was provided to enhance illumination. A digital camera was also bench-mounted and set to capture images of the suspension front.

Sedimentation rate (Rs) may be expressed, at low particle concentration, in discrete settling mode as Equation 1 according to Stokes (Nutan and Reddy, 2010).

$$Rs = \frac{dh}{dt} = \frac{d^2(\rho_1 - \rho_2)g}{18\mu} \qquad (1)$$

where Rs = sedimentation rate, d = diameter of the particle, ρ_1 = density of disperse phase, ρ_2 = density of dispersion medium, g = acceleration due to gravity and μ = viscosity of the dispersion medium.

When particle concentration is high, Stokes' equation may not show the real sedimentation rate. Vasilind and Dick and Young introduced equations 2 and 3 to accommodate suspensions with high particle content (Zhang *et al.*, 2015).

$$Rs = \frac{dh}{dt} = V_0 exp^{-nX} \qquad (2)$$

$$Rs = \frac{dh}{dt} = V_0 X^{-n} \qquad (3)$$

where Rs = sedimentation rate, V_0 = maximum sedimentation rate, X = solid concentration and n = sedimentation index.

The sedimentation behaviour of insoluble material (precipitate) from solution medium depends upon the concentrations of reacting species (Essien and Ekpe, 1998) .Changes in height (dh) against time (dt) were plotted as sedimentation rate curves for the determination of initial sedimentation rate (Rs). Plots of log (Rs) against log (ion species) determined other sedimentation characteristics.

RESULTS AND DISCUSSION
Variation of TCP and TSP Initial Sedimentation Rates with Temperature and Concentration:
Figures 1 to 4 express the results of initial sedimentation rates of TCP and TSP as functions of temperature at different metal and phosphate concentrations. They show that initial sedimentation rate is independent of temperature variation but is markedly influenced by low concentrations (<

0.04M) of metal and phosphate ions. Rise in temperature from 30 to 55^oC, gave poor negatively correlated (non-linear) initial sedimentation rate profiles of TCP and TSP for 0.02 and 0.04M metal and phosphate ions concentrations. Temperature effects leveled out completely from 0.06M and beyond, possibly due to high particle (precipitate) content. However, the results show that at the various temperatures, initial sedimentation rates of TCP and TSP were high at low concentration of both the metal and phosphate ions. For example, at 35^oC initial sedimentation rate of TCP (or TSP) decreased from (0.062 cms^{-1} to 0.010cms^{-1}) or (0.036 cms^{-1} to 0.018cms^{-1}) when calcium and strontium ions concentrations respectively increased from 0.02M to 0.04M. From 0.04M to 0.06M calcium or strontium ions concentrations, the initial sedimentation rates only dropped from (0.010 cms^{-1} to 0.007cms^{-1}) or (0.018 cms^{-1} to 0.009cms^{-1}). Similarly, when phosphate ions concentration increased from 0.02M to 0.04M, TCP (or TSP) precipitate initial sedimentation rate passed down from (0.068 cms^{-1} to 0.013cms^{-1}) or (0.072cms^{-1} to 0.041cms^{-1}). From 0.04M to 0.06M phosphate ions concentration, the initial sedimentation rates of TCP (or TSP) precipitate again only dropped from (0.013 cms^{-1} to 0.007cms^{-1}) or (0.041 cms^{-1} to 0.015cms^{-1}).By direct mixing, various degrees of particle concentration were created in the reaction vessel. High particle concentration promotes particle-particle interactions and results in hindered sedimentation (Punnamaraju, 2012; Mastropietro *et al.*, 2013); thus lower sedimentation rate. High temperature also enhances particle-medium interactions (Gary, 2004), which increased the tendency for the particles to remain stabilized at the initial precipitation stages. Solution-driven interactions of the precipitates with H^+ and OH^- of the aqueous medium (Bouchoud, *et al.*, 2010; Recillas, *et al.*, 2012) would also be high at high temperature. The visual observation employed did not give much clue on interactions except that at temperatures above 40^oC, it was observed that the haziness of the suspension mixtures (particularly the 0.02M concentration), as seen through the transparent settleometer, slightly decreased. Although, rising temperature also causes decrease in medium viscosity (Nutan and Reddy, 2010), it is likely that the degree of interactions (particle-particle and particle-medium) out-weighed the decrease of viscosity and sedimentation rate of precipitate, Rs, may be expressed as (Victor *et al.*, 2007):

$$R_s = K_s[M^{+2}]^{-a}[PO_4^{3-}]^{-b} \qquad (4)$$

The empirical sedimentation order (a) and sedimentation rate constant (Ks_M) with respect to the metal ions concentration were evaluated by keeping $[PO_4^{3-}]$ constant (or isolated) as:

$$R_{sM} = K_{sM}[M^{2+}]^{-a} \qquad (5)$$

Similarly, the empirical sedimentation order (b) and sedimentation rate constant (Ks_P) with respect to the

phosphate ions concentration were evaluated by keeping $[M^{2+}]$ constant (or isolated) as:

$$R_{SP} = K_{SP}[PO_4^{3-}]^{-b} \qquad (6)$$

Rs_M and Rs_P are the initial sedimentation rates of precipitates with respect to metal ions (Ca^{2+} or Sr^{2+}) and phosphate ions concentrations respectively.

Sedimentation Rate Parameters of TCP and TSP Precipitates: From the data obtained, the other sedimentation characteristics of TCP and TSP (Tables 1 and 2) indicate that, at constant phosphate ions concentration, sedimentation order with respect to metal ions (a) ranged between 0.63 and 1.23 for TCP and 0.58 and 1.31 for TSP. Also, at constant metal ions concentration, sedimentation order with respect to phosphate ions concentration (b) ranged between 1.52 and 2.10 for TCP and 1.55 and 1.81 for TSP.
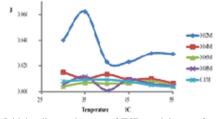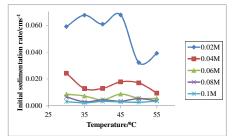

Fig 1: Initial sedimentation rate of TCP precipitate as function of temperature for various $[Ca^{2+}]$.

Fig 2: Initial sedimentation rate of TCP precipitate as function of temperaturefor various $[PO_4^{3-}]$.
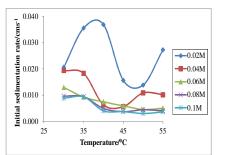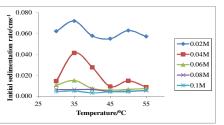

Fig 3: Initial sedimentation rate of TSP precipitate as function of temperature for various $[Sr^{2+}]$.

Fig 4: Initial sedimentation rate of TSP precipitate as function of temperature for various $[PO_4^{3-}]$.

The empirical sedimentation order and sedimentation rate constant (Tables 1 and 2) gave no linear correlation with temperature. This suggest that the order and rate constant of sedimentation cannot be predicted by temperature variations; their values may depend on the nature of the precipitant ions forming the precipitate and the size (colloidal) of the precipitate particle formed. In an earlier study on magnesium and calcium carbonate sedimentation, Obunwo *et al.,* (2014) suggested that the sedimentation rate constant was an intrinsic property which depended among others factors, on the nature of precipitate formed.

Table 1: Kinetic Parameters on the Sedimentation of $Ca_3(PO_4)_2$ precipitate at different Temperatures

Temperature, °C	Sedimentation Order (a) at constant $[PO_4^{3-}]$	Sedimentation Rate Constant, ks_{Ca}, at constant $[PO_4^{3-}]$ cms⁻¹M	Sedimentation Order (b) at constant $[Ca^{2+}]$	Sedimentation Rate Constant ks_P, at constant $[Ca^{2+}]$ cms⁻¹M
30	1.21	2.89×10^{-4}	1.78	6.32×10^{-5}
35	1.11	5.11×10^{-4}	2.10	1.71×10^{-5}
40	1.21	2.01×10^{-4}	1.83	3.98×10^{-5}
45	0.63	1.57×10^{-3}	2.01	2.73×10^{-5}
50	1.07	4.04×10^{-4}	1.52	9.54×10^{-5}
55	1.23	1.80×10^{-4}	1.53	8.51×10^{-5}

Table 2: Kinetic Parameters on the Sedimentation of $Sr_3(PO_4)_2$ precipitate at different Temperatures

Temperature, °C	Sedimentation Order (a) at constant $[PO_4^{3-}]$	Sedimentation Rate Constant ks_{Sr}, at constant $[PO_4^{3-}]$ cms⁻¹M	Sedimentation Order (b) at constant $[Sr^{2+}]$	Sedimentation Rate Constant ks_P, at constant $[Sr^{2+}]$ cms⁻¹M
30	0.58	2.45×10^{-3}	1.59	1.12×10^{-4}
35	0.90	9.67×10^{-4}	1.77	9.16×10^{-5}
40	1.28	1.82×10^{-4}	1.81	5.70×10^{-5}
45	0.88	4.37×10^{-4}	1.60	7.89×10^{-5}
50	0.98	3.43×10^{-4}	1.72	6.40×10^{-5}
55	1.31	1.51×10^{-4}	1.55	9.75×10^{-5}

*Conclusion***:** We have studied the effects of temperature and ion concentration on the initial sedimentation rates of TCP and TSP precipitates by the method of initial rate. It was found that initial sedimentation rate is independent of temperature variation but is markedly influenced by low concentrations ($< 0.04M$) of the metal and phosphate ions. The sedimentation orders and sedimentation rate constants of TCP and TSP showed no dependence on temperature. The nature and concentration of ions, size (colloidal) of the particle, high particle content, particle-particle and particle-medium interactions affect initial sedimentation rate of precipitates. Data may be useful as additional design information for modeling temperature and concentration variations for physiochemical phosphate removal in water treatment technology.

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