Critical flocculation concentration for polyvalent ions using silica nanoparticles; a new version of Schulze-Hardy rule

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Abstract
Critical Flocculation Concentration (CFC) is an important quantity because allows to know the optimal amount of flocculant required to remove (adsorb) specific quantities of metal ions in aqueous solution allowing to reduce both, the flocculation time and the excess of unreacted flocculant; this unreacted material produces, by itself, an additional contamination. The results reported here show that the standard Schulze-Hardy-Rule (SHR), based only in the valence z, is not longer valid to obtain the right values of CFC. In this work it is reported a correct determination of CFC for di- and tri-valent ions using different types of silica nanoparticles. Both, the initial pH slope (-pH_o) and the valence z are required to determine correctly the CFC. The proposed modified version for CFC is $CFC \propto \frac{(-pH_o)^z}{C_0}$.

Keywords
Adsorption, flocculant, CFC, Schulze-Hardy-Rule, industrial wastes

Submission date: 11 July 2020; Acceptance date: 19 August 2020

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Introduction

The removal of heavy metal ions from water bodies contaminated by industrial wastes, is an important health problem because the reserves of drinkable water are reducing drastically by the increment in the population and in the industrial activity (Joseph et al., 2019; Mishra et al., 2020); in addition to this is the high toxicity of these ions which affect the human health, living resources and ecological systems, including groundwater contamination; consequently the remediation of these contaminated water bodies is highly recommended and urgent (Vardhan et al., 2019). Water contamination by organic matter is not as severe as by metals ions, particularly by heavy metals ions; this is because the organic matter can be transformed in innocuous compounds by chemical or biological process (Abdullah et al., 2019; Anastopoulos et al., 2019; Huang et al., 2019; Yadav et al., 2019); however, heavy metals can not be transformed by any known method into a no-toxic compounds. The high toxicity and the accumulating effect of these ions affect all living creatures included human beings producing severe harmful effects (Ayangbenro and Babalola, 2017; de Angelis et al., 2017; Klein, 2019; Mehmood et al., 2019). The removal of metal ions is difficult because microorganism does not process them and the filtration processes are not appropriated due to the small size (Cai et al., 2019).

The contamination of untreated industrial wastewater exceeds, in most cases, the legal limits officially stated. The most toxic heavy metals are Cd, Hg, Pb (Gholizadeh et al., 2019; Wu et al., 2018); the maximum permissible concentrations of these metals in drinkable water has been established by several international world organizations: for World Health Organization (WHO), “Guidelines for Drinking-Water Quality” (2006), the limits are: 3 ppb for Cd, 6 ppb for Hg, 10 ppb for Pb; for Al the limit is 200 ppb (Jamshaid et al., 2018). For the Comprehensive Environmental Response Compensation and Liability Act (CERCLA), USA, the limits are: 50 ppb for Cd, 15 ppb for Pb, 2 ppb for Hg. These heavy metal ions have not any biological function for living beings (Becerra-Castro et al., 2015; Chaoua et al., 2019; El-Kady and Abdel-Wahhab, 2018; Johnson, 1998; Menon et al., 2016; Tamim et al., 2016). Al was included first because is the only trivalent cation considered here, and second because it is the most abundant metal on earth and posses a wide range of industrial applications; consequently, the people has a significant contact it and this metal is not present in the human body (Ramrakhiani et al., 2017; Savvilotidou et al., 2014).

In recent years the bioremediation, using microbial as biosorbents, has attracted considerable attention in detriment of physicochemical methods. It is claimed that the physicochemical methods are not economically viable, producing a considerable amount of sludge and the legal limits are not reached (Zhou et al., 2018); on the other side, the advantages of bioremediation are: it is environment-friendly and produces small amounts of sludge, it is economically viable and efficient to remove heavy metals (Jiang et al., 2019). However, it is important to mention that the microbial do not transform the heavy metals into innocuous compounds; the majority of heavy metals disrupt the microbial cell membranes and they are released contaminating the sludge. There are different ways the microbial deal with heavy metals; it has been reported that they produce metal chelating substances to isolate the heavy metals (Ayangbenro and Babalola, 2017). It has been also reported that the metal ions are fixed in the intracellular region reducing the potential damage to the cell.

Most microorganisms have, on their surfaces, some chemical groups (hydroxyl or carboxyl) that can adsorb the metal ions releasing hydrogen (Jiang et al., 2019, Xue et al., 2018, Zhang et al., 2019); this is an efficient way to adsorb ions because a strong ionic chemical
bond is formed. However, this process is very similar to the adsorption of metal ions using nanoparticles with the appropriated chemical groups on their surfaces (Burakov et al., 2018); even when the internal mechanisms for these two methods are not the same, the final effect is very similar: adsorb ions for future removal.

Despite all these similitudes there are some important differences between the use of microbial respect to the use of inorganic nanoparticles for the adsorption of metal ions: a) at the final step, when it is required to isolate permanently the metal ions, the use of silica nanoparticles allows this permanent isolation just by rising the temperatures to obtain a vitreous matrix doped with the removed metals, while in the microbial case an increment in temperature destroy the organic matter releasing the metals ions and contaminating the surrounded region; b) because the commercial silica nanoparticles are dense and rigid with different chemical groups on their surfaces, once the metal ions are adsorbed the sludge produced is compact and easy to remove; this is not the case for microbial or hydrophilic polymers which produce loose sludge with poor consistency: the microbial are hydrophilic soft structures producing no-compact sludge difficult to handle; c) the silica nanoparticles posses extremely high surface area (more than 100 m²/g) with different chemical groups to adsorb large quantities of metal ions; this is not the case for microbial with low surface area; d) the inorganic nanoparticles are available in large quantities with a extremely large shelf-time; this is not the case for microbial where the shelf-time is reduced requiring special and stringent storage conditions; e) the silica nanoparticles have a very reproducible characteristics while microbial are extremely dependent of the production process; f) the inorganic nanoparticles are relatively inexpensive respect to microbial, allowing to deal with large volume of wastewater at low price; g) it is not required a special infrastructure to use the nanoparticles while the bacterial requires special ones; h) the silica nanoparticles are insensitive to external conditions (weather, temperature, etc.) while this is not the case for microbial; i) the handling of nanoparticles is safe and no-toxic, but this is generally no true for microbial; j) the silica particles are very stable, while the bacterial are easily contaminated by strange substances; k) typical silica particles are appropriated for all metal ions, however special strains are required for each heavy metal (Afkhami et al., 2010; Atasoy and Bilgic, 2018; Najafi et al., 2012; Rostamian et al., 2011). For these reasons, silica nanoparticles were selected as an excellent option for the removal of heavy metal ions from industrial wastewater.

What is really required in the use of inorganic nanoparticles is to optimize the physicochemical method to reduce, as much as possible, the amount of adsorbent (nanoparticles) without to sacrifice the efficiency in the adsorption: to use an excess of adsorbent produces contamination of the water and an increment in the cost of the process; a deficiency of absorbent give place to an incomplete adsorption, leaving metal ions in the wastewater. In order to have an optimal and efficient process it is required knowledge of the CFC because this quantity gives information about the minimum amount of flocculant required to remove specific concentrations of metal ions without any additional contamination. The SHR provides, in principle, a method to determine CFC knowing only the ions' valence $z$: $CFC \propto z^{-6}$ (Hiemenz and Rajagopalan, 1997). However, the results presented here show that this rule is not longer valid essentially because the initial pH slope ($pH_o$) of the systems was not taken into account together with the valence $z$. A new proposal is made where the CFC can be correctly determined using the product ($-pH_o$)$z$, i.e. $CFC \propto [(-pH_o)z]^{-1}$. This proposal was tested by analyzing the adsorption of di- and tri-valent ions in solution ($Al^{3+}$, $Cd^{2+}$ and $Pb^{2+}$) using different types of silica nanoparticles.
Methodology

Silica nanoparticles

Two types of commercial silica nanoparticles were used as adsorbent: a) Aerosil A130VS (Degussa, AG) and b) Aerosil R972 (Degussa, AG); additionally the A130VS nanoparticles were modified with TEOS using the sol-gel method (Hernández and Rodríguez, 1999) to increase the number of OH groups on the surface and consequently its adsorption capacity; this reaction can be schematically written as:

\[
\text{A130VS} + \text{OH} + \frac{1}{2} \text{Si} - (\text{O} - \text{CH}_2 - \text{CH}_3)_4 + 3\text{H}_2\text{O} \rightarrow \\
\text{A130VS} - \text{O} - \text{Si} - (\text{OH})_3 + (\text{CH}_3 - \text{CH}_2 - \text{OH})_4
\]

In principle, each OH group in the nanoparticle can be increased by a factor of three using TEOS however, due to the steric effects, the average number of OHs is practically incremented at double. All silica nanoparticles were kept for one day in distilled water for hydration which produces silanol groups: \(\equiv\text{Si-O-Si}\equiv + \text{H}_2\text{O} \rightarrow 2(\equiv\text{Si-OH})\).

The Aerosil A130VS is amorphous fume and dense silica particles with hydrophilic silanol groups \((\equiv\text{Si-OH})\) on the surface and with a nominal average primary size of 16 nm. The average surface area, determined by BET, was of \((130 \pm 25)\) m\(^2\)/g with 1.3 Si-OH groups/nm\(^2\) (Bode et al., 1997). The Aerosil R972 is also amorphous fumed and dense silica with nominal size of 16 nm and has, in addition to the hydrophilic OH groups, hydrophobic dimethyl silyl groups (-SiH=-(CH\(_3\))\(_2\)) on the surface; the methyl groups block active sites for the adsorption of metal ions. The average surface area, determined by BET, was of \((110 \pm 20)\) m\(^2\)/g and they have 0.60 hydrophilic (\(\equiv\text{Si-OH}\)) groups/nm\(^2\) and 2.7 hydrophobic (CH\(_3\)) groups/nm\(^2\).

Samples preparation and flocculation procedure

The silica sol was prepared as reported elsewhere (Vargas et al., 2015): filtered (2.0 \(\mu\)m nylon membrane) alkaline water (pH = 11) was prepared using ammonium hydroxide (Baker, Co.). 1 g of each type of nanoparticles was dispersed, separately, in 100 mL of alkaline water (concentration of \(10^{-2}\) g/mL) during 24 h with mild agitation; these are the silica sols. Six dilutions of each type of nanoparticles were prepared by mixing 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mL of silica sol with 7 mL of distilled and filtered water at neutral pH given place to the following corresponding concentrations: 0.7, 1.4, 2.1, 2.8, 3.6 and 4.3 mg/mL. Three stock aqueous solutions of metal ions (Al\(^{3+}\), Cd\(^{2+}\), Pb\(^{2+}\)) at 1000 ppm were prepared from nitrate (Aldrich Co.) and used as metal sources.

Small volumes of metal ions \((V_{\text{ion injected}})\) were injected to the silica sol every three minutes until the system flocculate. For the sample containing 0.5 mL of silica sol, each injection of ions was of 0.05 mL, i.e. 0.05 mg of ions; for the other systems the injections were of 0.1 mL, i.e. 0.1 mg of ions. After each injection, the system was mildly stirred for few seconds for homogenization. Because the rate of ions’ addition, \(rate_{\text{ion injected}}\), is constant:

\[
rate_{\text{ion injected}} = \frac{V_{\text{ion injected}}}{t} \Rightarrow V_{\text{ion injected}} = \left(\frac{rate_{\text{ion injected}}}{t}\right)t
\]

(1)
the volume of injected ions, $V_{\text{ion}}^{\text{injected}}$, grows linearly with the time: for 0.5 mL of silica particles $\text{rate}_{\text{ion}}^{\text{injected}} = 2.78 \times 10^{-4} \text{mL/s}$ and for 1.0–3.0 mL of silica particles $\text{rate}_{\text{ion}}^{\text{injected}} = 5.56 \times 10^{-4} \text{mL/s}$.

The silica particles are stable in alkaline water however, in presence of metal ions these are adsorbed and the particles release $H^+$ reducing the pH and making unstable the dispersion; this produces aggregates of nanoparticles which, eventually, sediment. The size of the aggregates and the aggregation kinetics were determined using Dynamic Light Scattering (DLS) (Brookhaven Instr Corp, model BI200SM) (Vargas et al., 2015). The sediment, containing the metal ions, was separated by centrifugation (2000 rpm during 60 min), decanted, washed twice with distilled water, digested (10 mL of nitric acid, 10 mL of hydrochloric acid and 0.5 mL of hydrofluoric acid) in a Teflon container using a microwave oven (CEM model MDS-2100) for 20 min, cooled to room temperature, filtered (Whatman No 41), diluted in 50 mL of distilled water and injected in the Atomic Absorption (AA) apparatus (Varian model SpectrAA 20) to determine the amount of metal ions removed from water. This procedure was repeated three times and the average values are reported. The AA apparatus was calibrated using SPEX analytical grade standards. The error in the adsorption is below 0.5%.

**Extended version of the Schulse-Hardy rule**

The SHR states that the valence of the ions of opposite charge to the colloidal particles (counterions) is the most important characteristic for the colloidal stability: the greater is the valence, the faster is the flocculation (Hiemenz and Rajagopalan, 1997); the valence determines the CFC according to:

$$\text{CFC} \propto z^{-6} \quad (2)$$

i.e. trivalent ions can aggregate more efficiently charged particles respect, for example, to divalent ones; this is the Schulze-Hardy Rule. Even when the $z$-dependence is necessary, it is not sufficient; CFC must depend, in addition to $z$, to the negative initial pH slope (-pH$_o$) defined as. (-pH$_o$) $\equiv -\left(\frac{d\text{pH}}{dV_{\text{ions}}}\right)_o$, i.e. the change of pH respect to the ions injected volume.

When this quantity is included together with $z$, it is possible to determine correctly the CFC for other systems.

The important quantity required to determine correctly CFC is the product (-pH$_o$)$z$. For the flocculation processes reported here, the pH profiles have an initial linear region with a negative constant slope (-pH$_o$) then, the product (-pH$_o$)$z$ is constant for each profile but it is different from one profile to another; this set of constants will be denoted by $x_i$ where the index $i$ labels each profile. The product (-pH$_o$)$z$, for the i-profile, can be written as:

$$-\left(\frac{d\text{pH}}{dV_{\text{ions}}}\right)_i z_i = (-\text{pH}_o)_i x_i \propto x_i \quad (3)$$

however

$$(-\text{pH}_o)_i x_i \propto x_i \Rightarrow \frac{(-\text{pH}_o)_i x_i}{x_i} = \text{cte} \quad (4)$$

where cte is a constant.
From equation (4) it is possible to write:

\[
\frac{\alpha_i}{z_i} = \frac{\alpha_j}{z_j}
\]

(5)

For example, for Cd and Al:

\[
\alpha_{\text{Cd}} = \alpha_{\text{Al}} \left( \frac{\alpha_{\text{Cd}}}{\alpha_{\text{Al}}} \right) \left( \frac{Z_{\text{Cd}}}{Z_{\text{Al}}} \right)
\]

(6)

Then, using equation (5) it is possible to obtain the right values for \( \alpha \) knowing one value.

In the modified version of SHR, \( z \) was replaced by the product \((-pH_o)z\), i.e.

\[
\text{CFC} \propto [(-pH_o)z]^{-n} \propto \alpha^{-n}
\]

(7)

The exponent \( n \) can be determined as follows: from Figures 2 to 4 it was possible to obtain CFC as a function of \((-pH_o)z\); this is reported in Figure 5 for Al and Cd; the curves were fitted using a power law: \( \text{CFC} = A[(-pH_o)z]^n \) where the exponents for Al and Cd are, respectively \( n = -1.041 \) and \( n = -1.055 \). Then, the exponent in equation (7) was set to \( n = -1 \), i.e. CFC can be written as. \( \text{CFC} = A[(-pH_o)z]^{-1} \) where \( A \) is a constant. The final expression for SHR-m is:

\[
\text{CFC} \propto [(-pH_o)z]^{-1} \propto \alpha^{-1}
\]

(8)

Old SHR version: \( \text{CFC} \propto z^{-6} \). New (SHR-m) version: \( \text{CFC} \propto [(-pH_o)z]^{-1} \propto \alpha^{-1} \)

**Results**

Figure 1 shows the flocculation profiles of Al\(^{3+} \) ions using VS nanoparticles; for other ions and particles the profiles (no shown) are similar. From the flocculation profiles it is possible to determine the CFC. For Al\(^{3+} \) in VS and VS+TEOS the CFCs are reported in Figure 2; similar plots (no-reported) were obtained for other systems.

The addition of metal ions to the silica sol reduces the pH by the production of H\(^+ \). Figure 3 shows typical pH profiles obtained as a function of the injected volume \( V_{\text{injected}} \) of Al\(^{3+} \) ions to VS particles. In Figure 4 is plotted the negative of the initial slope \((-pH_o)\) of the profiles reported in Figure 3, as a function of silica volume \( V_{\text{silica}} \) for Al\(^{3+} \) using VS nanoparticles; these data were fitted (the continuous line) using a second order kinetics:

\[
r = \frac{r_0}{(1 + r_0kt)}
\]

(9)

where \( r \) is the reactant concentration at time \( t \), \( r_0 \) the initial reactant concentration and \( k \) the reaction velocity. The fitting produces: \( r_0 = 32.3 \) and \( k = 1.16 \times 10^{-3} \) s\(^{-1} \).
Figure 1. Flocculation profiles of $\text{Al}^{3+}$ ions using VS nanoparticles.

Figure 2. CFC for $\text{Al}^{3+}$ in VS and VS+TEOS as function of $C/C_1$ ($C_1 = 0.71 \text{ mg/mL}$).
Discussion

In the flocculation profiles reported in Figure 1 it is possible to observe two regimes: the first one shows a slow increment in the size of the aggregates corresponding to a primary flocculation; the second one shows a fast increment in the size of the aggregates and it is called secondary flocculation. In the first case the aggregation corresponds to the addition of single nanoparticles practically one at a time, while the second one corresponds to aggregation of aggregates. In the first regime the aggregation process is slow and, consequently, the pH reduces also slowly in a linear way; the initial pH slope is denoted by \((-\text{pH}_0)\) which is a positive quantity because the slope is negative. The last regime happens when the pH has reached low values destabilizing the suspension and allowing the flocks approach each other to form greater structures. The transition between these two regimes corresponds to CFC.

From Figure 2 it is possible to observe that CFC follows a linear relationship with the silica volume \(V_{\text{silica}}\); these curves provide information on the minimum amount of flocculant needed to adsorb the ions; for example from this figure it is possible to see that 1 mL of VS...
or VS+TEOS was required to flocculate 0.30 or 0.41 mg/mL of Al$^{3+}$ ions, respectively. This shows clearly the importance of CFC to have an optimal flocculation process without further contamination.

The pH profiles are reported in Figure 3. These show two regimes: in the first one the pH reduces linearly with the volume of injected ions, $V_{\text{ion}}$, while in the second one the pH reduces rapidly. Because $V_{\text{ion}}$ increases linearly with the time (equation (1)), the H$^+$ production also increases linearly and, consequently, the pH reduces linearly with the time and with $V_{\text{ion}}$, i.e. $(-pH_o) \equiv \left( \frac{dpH}{dV_{\text{ion}}} \right)$; this is the reason of the linear pH reduction in the first part of the profiles. These initial slopes $(-pH_o)$ together with the valence $z$, provide the complete information required to determine CFC and the aggregation kinetics (Medina et al., 2010; Pacheco et al., 2006).

In Figure 4 is reported a plot of $(-pH_o)$ as a function of silica volume $V_{\text{silica}}$. The initial pH slope $(-pH_o)$ measures the rate of pH reduction as a function of $V_{\text{ion}}$; this reduction is due to the H$^+$ production that is closely related to the adsorption process. Then, according to this it is possible to say that the adsorption follows a second order kinetics: $r = \frac{r_o}{(1 + r_o k t)}$ where the values for $r_o$ and $k$ are: $r_o = 32.3$ and $k = 1.16 \times 10^{-3}$ s$^{-1}$.

The curves in Figure 5 correspond to CFC versus $(-pH_o)z$ for Al$^{3+}$ and Cd$^{2+}$ in VS nanoparticles. The fittings were performed according to a power law: $\text{CFC} = A[(-pH_o)z]^n$ where, for Al CFC $= 4.29 [(-pH_o)z]^{-1.04}$ and for Cd CFC $= 7.88 [(-pH_o)z]^{-1.06}$. As can be noticed, both exponents are very near to one, i.e. $\text{CFC} = A[(-pH_o)z]^{-1} \propto z^{-1}$. This is the expression obtained for SHR-m.
The substitution of \( z \) by \((-pH_O)z\) in the SHR-m, provides a proper scheme for the correct determinations of \( \alpha \) parameters which are directly related to CFC. Equations (4) or (5) gives a good estimation of the \( \alpha \) values, knowing just one; knowing CFC it is possible to design an optimal flocculation process with a minimum amount of unused flocculant and the minimum time for the process.

It is possible to observe, from the results reported in Figure 6, that neither the initial slopes nor the valence provide right values of CFC as stated by SHR: different CFC's values for the same valence, different slopes for the same valence; there is not an apparent correlation between these quantities. From this figure, in the first regime, there are straight lines with different slopes: for \( Al^{3+} \)–VS, \(-6.24\), for \( Pb^{2+} \)–VS, \(-4.95\), for \( Cd^{2+} \)–R972, \(-1.53\), for \( Cd^{2+} \)–VS, \(-1.46\). However, once the initial pH slopes were included together with the valence \( z \), there is a strong correlation between these values.

Equation (5) is the mathematical expressions that allows to calculate the \( \alpha \) parameter for different systems knowing one \( \alpha \) parameter. Using this equation and knowing, for example \( \alpha_{Al} \), it is possible to calculate \( \alpha_{Cd} \) and \( \alpha_{Pb} \) for different types of nanoparticles. From Figure 6 for \( Al^{3+} \) (VS), \( \alpha_{Al} = 6.24 \), \( (pH_O) = 7.34 \) and \( z_{Al} = 3 \). From these values it is possible to obtain: for \( Cd^{2+} \) (VS) and \( (pH_O) = 2.38 \), \( \alpha_{Cd} = 1.350 \); for \( Cd^{2+} \) (R-972) and \( (pH_O) = 2.85 \), \( \alpha_{Cd} = 1.615 \); for \( Pb^{2+} \) (VS) and \( (pH_O) = 7.95 \), \( \alpha_{Pb} = 4.506 \). The calculated values are very close to those reported in Figure 6: for Cd (VS) \( \alpha_{Meas} = 1.46 \) and \( \alpha_{Calc} = 1.35 \); for Cd (R972) \( \alpha_{Meas} = 1.53 \) and \( \alpha_{Calc} = 1.62 \); for Pb (VS) \( \alpha_{Meas} = 4.95 \) and \( \alpha_{Calc} = 4.51 \). For clarity and comparison, a summarize of the measured and calculated \( \alpha \) values for different ions and nanoparticles is reported in Table 1.
Figure 6. Initial slope (-pH₀) for all ions and nanoparticles as a function of C/C₁ (C₁ = 0.71 mg/mL).

Figure 7. Adsorption of Pb²⁺, Al³⁺, Cd²⁺ as a function of C/C₁ (C₁ = 0.71 mg/mL).
The small discrepancies between the measured and calculated $x$ values may be due to the relative sizes of the particles and aggregates respect to the ions: it is difficult for a very small trivalent ion, like $\text{Al}^{3+}$, put together three large silica particles to form the aggregates; this is mainly due to the strong steric hindrance effects. The ionic radii are: 0.54 Å for $\text{Al}^{3+}$, 0.95 Å for $\text{Cd}^{2+}$ and 1.19 Å for $\text{Pb}^{2+}$ and the nanoparticles have 16 nm; the steric effects become stronger and more important for ions of high valence and small size. Additionally, the nanoparticles must have the appropriated chemical groups on the surface to provide strong bonds and stable aggregates.

The adsorption results for $\text{Al}^{3+}$, $\text{Cd}^{2+}$ and $\text{Pb}^{2+}$ using different types of silica nanoparticles are reported in Figure 7: for $\text{Cd}^{2+}$ the adsorption was 100% (2.0 mL of VS) and 99.7% (1.5 mL of R-972); for $\text{Al}^{3+}$ the adsorption was 99.4% (0.5 mL of VS) and 97.4% (2.0 mL of VS+TEOS); for $\text{Pb}^{2+}$ the adsorption was 99.3% (1.5 mL of VS) and 98.2% (2.0 mL of VS+TEOS). $\text{Cd}$ is an ion easy to adsorb because it has a considerable large size allowing an easier bridging between nanoparticles. $\text{Pb}^{2+}$ and $\text{Cd}^{2+}$ have similar adsorptions because both have similar size. A summarize of the ions’ removal using different concentrations and types of nanoparticles are reported in Table 2.

### Conclusion

High adsorption values were obtained for: $\text{Cd}^{2+}$, $\text{Pb}^{2+}$ and $\text{Al}^{3+}$, using different types of silica particles: VS, VS+TEOS, R-972. The adsorption values are: for $\text{Cd}^{2+}$ was 100% with 2.0 mL of VS, and 99.7% with 1.5 mL of R-972; for $\text{Al}^{3+}$ was 99.4% with 0.5 mL of VS and 97.4% with 2.0 mL of VS+TEOS; for $\text{Pb}^{2+}$ was 99.3% with 1.5 mL of VS and 98.2% with 2.0 mL of VS+TEOS. The modified version of SHR allows to obtain important parameters to optimize flocculation processes. In the primary regime the important quantity is the
product of the valence \( z \) and the initial pH slope \((-pH_o)\), i.e. \((-pH_o)z\). In the flocculation processes reported here the pH profiles have an initial linear region with a constant slope, then, \( \frac{(-pH_o)z_i}{C_0} = \text{cte} \); from this expression it is possible to write for CFC the expression: \( \text{CFC} \propto \left[(-pH_o)z\right]^{-1} \propto z^{-1} \). This expression was supported from the flocculation results using di- and tri-valent ions and different types of silica particles. Using these equations and choosing, for example, \( \text{Al}^{3+} \) in VS as a reference, \( \alpha_{Mea} = 6.24 \) and \( (pH)_o = 7.34 \), it was possible to obtain:

- for \( \text{Cd}^{2+} \) (VS) \( \alpha_{Cd}^{\text{Calc}} = 1.35 \) and \( \alpha_{Cd}^{\text{Mea}} = 1.46 \); for \( \text{Cd}^{2+} \) (R-972) \( \alpha_{Cd}^{\text{Calc}} = 1.62 \) and \( \alpha_{Cd}^{\text{Mea}} = 1.53 \); for \( \text{Pb}^{2+} \) (VS) \( \alpha_{Pb}^{\text{Calc}} = 4.51 \) and \( \alpha_{Pb}^{\text{Mea}} = 4.95 \); the calculated values are very close to measured ones. SHR-m provides a right estimation of the calculated \( \alpha \) values as compared with the measured ones with high accuracy. The SHR-m which is expressed as \( \text{CFC} \propto \left[(-pH_o)z\right]^{-1} \propto z^{-1} \), has a structure similar to SHR but conceptually are completely different. The corrected values of CFC allow to design optimal flocculation process using the minimum amount of flocculant.

**Highlights**

- Adsorption of trivalent ions by nanoparticles
- Hydrophobic and hydrophilic nanoparticles for metal adsorption
- Dependence of the adsorption with the valence of the ions
- Comparative study using ions with different valence

**Declaration of Conflicting Interests**

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

**Funding**

The author(s) received no financial support for the research, authorship and/or publication of this article.

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**Supplemental Material**

Supplemental material for this article is available online.

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