Removal of water hardness from aqueous solution by BaCO₃ nanoparticles

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Abstract:

The present study reports the water softening by removal of hardness producing ions using barium carbonate nanoparticles (BaCO₃ Nps). BaCO₃ Nps were synthesized by the PVP-assisted precipitation method. The synthesized nanoparticles were characterized by Fourier transform infrared (FT-IR) spectroscopy, X-ray powder diffraction (XRD), Scanning electron microscope (SEM), and Dynamic light scattering (DLS) analysis. The aptitude of the BaCO₃ Nps for removal of hardness from aqueous solution has been investigated by ion exchange chromatography. Effect of various parameters viz. contact time, pH effect (pH 2–10), dose of nanoparticles (0.01–0.1 g/100 ml), initial calcium and magnesium concentration (0.01–10 mg L-1) and effect of competitive ions has been investigated to determine the hardness removal capacity of BaCO₃ nanoparticles. Results of kinetic data correlated well with the pseudo-second-order kinetic model, indicate that the chemical adsorption is the rate limiting step. Thermodynamic parameters show that the removal process is spontaneous and endothermic in nature. Isotherm data suggested that not only adsorption but precipitation transformation mechanisms playing a key role in the removal of hardness respectively.

Keywords

nanoparticles, hardness, ion-exchange, adsorption isotherm

1. Introduction

Water is the primary fundamental component on the earth for life-sustaining activities. Unfortunately, water quality of natural water resources is degenerating continuously due to geological and environmental changes and by many simulated activities like industrialization, civilization, domestic and agricultural activities and others [1−3].

Therefore, water treatment has become a vital necessity in the present scenario because it has unswervingly affected on all living creatures, domestic and other commercial activities [4−6]. Water contaminates by thousands of organic, inorganic, and biological pollutants [7]. Many inorganic metal ions are notorious water pollutants with high toxicity and carcinogenicity [8-14].

Recently, nanomaterials have shown significance results due to their elevated effectiveness in water treatment than traditional materials, many reports revels the importance of the metal metal oxide, nanomaterials in the area of water treatment , such as iron-oxide, MnO₂ nanoparticles,[15]. In addition, carboxy methyl cellulose grafted on multiwalled carbon nano-tubes, [16] magnesium silicate hollow nano structures [17] and mesoporous F-TiO hollow microspheres [18] and CaO nanoparticles [19], have also shown better adsorption capacities than commercial adsorbents . All of these materials could rapidly remove toxic contaminants with a high elimination capacity due to their high surface area, facile mass transportation and abundant active adsorption sites. However, these materials are not used commercially due to the production cost and inconvenience method for product development. Hence, there is the huge demand of highly proficient and low-cost material for viable application.

From an economic perspective, metal carbonates are cheapest and abundant minerals in nature. Barium carbonate (BaCO₃) has an orthorhombic crystalline structure, and it is the most thermodynamically stable among the heavy metal carbonates. It is widely used for the production of barium salts, pigments, optical glasses, plastics, rubbers, and ceramics [20]. The BaCO₃ matrix has found very interesting NOₓ storage-reduction applications [21]. However, the risks associated with high concentrations of barium in the treated water and long retention time for hardness removal limited the use of barium salt [23-27].

The objective of this work is development of BaCO₃ nanoparticles and evaluates the potential of them; for the elimination of permanent hardness from water, to assess the permanent hardness removal we estimate the removal of Mg^{+2} and Ca^{+2} from water. In the present study have also evaluated the mode of action of BaCO₃ nanoparicles for removal of the permanent hardness (Mg^{+2} and Ca^{+2})

removal using $BaCO_3$ nanoparticles. Effect of competitive ions in the aqueous solution has also been investigated.

2. Experimental Methods

All chemicals used for this project were analytical reagent grade (AR) quality and used without further purification. During the complete work de-ionized and double distilled water has been used. Barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$), sodium carbonate (Na_2CO_3), sodium sulfate ($NaSO_4$), calcium chloride anhydrous ($CaCl_2$) and magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) were acquired from Aldrich. Polyvinyal pyrolidone, HCl and NaOH were obtained from Merck.

Synthesis of PVP stabilized BaCO3 nanoparticles

In a typical experiment, 5 ml of 0.1 M Na_2CO_3 solution and 10 ml of PVP (1 mg/ ml) aqueous solution were mixed under vigorous stirring for 30 minutes. 2 M NaOH had been used to adjust the pH about 9.0. Consequently, 5 ml of 0.2 M $BaCl_2$ was added drop wise to the above mixture with continuous stirring. White precipitate was formed during the addition. These precipitates were collected and washed with distilled water and methanol and dried in a vacuum (60ºC) for further analysis.

Physicochemical characterization of BaCO₃ nanoparticles

Development of $BaCO_3$ nanoparticles were assessed by FTIR spectrometer (JASCO FT/IR-4000). Conventional KBr disc method had been used. All the samples scanned between 400 and 4000 cm^{-1} Hydrodynamic diameter of $BaCO_3$ nanoparticles were examined by dynamic light scattering (DLS: Microtrac-NanotracTM 10.5.2.). Briefly, a dilute suspension of $BaCO_3$ nanoparticles were prepared in Milli-Q water and sonicated in bath sonicator for 30 seconds. Particle size was determined using software Microtrac FLEX.

Removal of magnesium and calcium ions

Standard 100 mg/ L of Ca^{+2} and Mg^{+2} solutions have been used as a stock solutions for hardness removal (Ca^{+2} and Mg^{+2}) experiments. The experiments were carried out by adding 0.01–0.10 g of $BaCO_3$ Nps in 100 ml of 100 mg /L Ca^{+2} and Mg^{+2} solutions in 250 ml PVC flask and continuous stirring on magnetic stirrer, at about 400 rpm for a predetermined time interval . All the experiments were carried out at ambient temperature (25 ± 1ºC). The solid particles in the mixture were separated by centrifugation and followed by filtration process. The concentration of Ca^{+2} and Mg^{+2} in filtrate were estimated by Dionex ion exchange chromatography system ICS 1000.

Each experiment was carried out twice to achieve reproducible outcome with more than 95% accuracy.

Results and Discussion

Preparation of BaCO3 nanoparticles

Table 1 summarizes the effect of the barium ion concentration, carbonate ion concentration, volume of PVP and reaction time on the particle size of the $BaCO_3$ particles precipitated via PVP-assisted route. It was observed that equal molar ratio of Ba^{+2}/ CO_3^{-2} gives desirable controlled size. Furthermore the volume of stabilizer also affects the size of nanoparticles. Low volume of the PVP cannot control the aggregation of nanopaticles and leads incrimination in size. In the case of high volume of stabilizer, PVP absorbs on the crystal of nanoparticles and step-up the size of nanoparticles.

Size of $BaCO_3$ nanoparticles was also affected by the time of the reaction, it was observed that low reaction time cannot manage the size of nanoparticles , it may be due to incompletion of the chemical reaction. Further it was observed that after 30 minutes, the reaction time did not have any effect on the size of the nanoparticles.

Physicochemical characterization of nanocarriers

The FT-IR spectrum of the BaCO3Nps is shown in Fig. 1a, which represents the classical peak of $BaCO_3$ Nps. In the spectra strong band at 1446 cm^{-1} and 866 cm-1 indicates the presence of $CO3^{-2}$. Further, band near 693cm^{-1} be a sign of the presence of inorganic element in sample. Also weak sharp band at 1060cm-1, support the presence of organometalic compounds [21].
Histogram of dynamic light scattering (DLS) analysis shows the narrow size distribution of the synthesized nanoparticles. It also illustrates the average diameter of $BaCO_3$ Nps were 69 ± 12 nm (Fig.1b).

Evaluation of hardness removal by BaCO₃ Nps

The main objective of this analysis was to study the removal of hardness in terms of removal of Mg^{+2} and Ca^{+2} ions by $BaCO_3$ Nps in different experimental condition such as nanoparticles dosage, contact time, pH and temperature. The experimental results and the important observations are discussed in the following sections.

Table 1. Process parameters of BaCO3 nanoparticles develpment

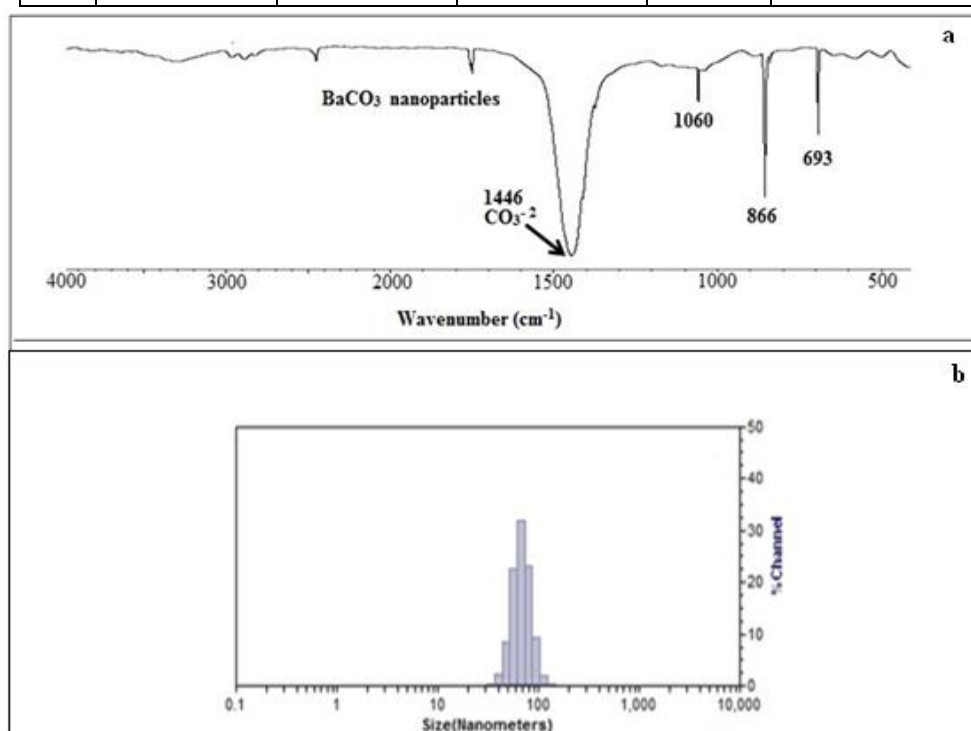| No.	$BaCl_2 \cdot 2H_2O$ Concentration	Na_2CO_3 Concentration	Volume of PVP (mg/ml)	Reaction time	Size of $BaCO_3$ nanoparticles
1	0.05 M	0.1 M	10	30	82 ± 30
2	**0.1 M**	**0.1 M**	**10**	**30**	**65 ± 10**
3	0.2 M	0.1 M	10	30	132 ± 25
4	0.1 M	0.05 M	10	30	110 ± 21
5	0.1 M	0.2 M	10	30	157 ± 32
6	0.1 M	0.1 M	5	30	146 ± 35
7	0.1 M	0.1 M	20	30	121 ± 15
8	0.1 M	0.1 M	10	15	113 ± 25
9	**0.1 M**	**0.1 M**	**10**	**45**	**69 ± 12**

Fig.1 (a) FTIR spectra (b) DLS histogram of $BaCO_3$

Effect of nanoparticles dosage

The effect of $BaCO_3$Nps dose on the removal of Mg^{+2} and Ca^{+2} were studied at ambient temperature (25 ± 2^oC) with 30 minutes of contact time. Initial concentration of Mg^{+2} and Ca^{+2} was 100 mg L^{-1}. The results have been presented in Fig.2 (a). It is reveals that the removal of Mg^{+2} increased from 19.4% to 98.8% and removal of Ca^{+2} increased from 12.4% to 63.2% with the increasing dosage of $BaCO_3$ Nps.

Effect of contact time

Fig.2(b) shows the effect of contact time on the removal of Mg^{+2} and Ca^{+2} by $BaCO_3$Nps. It is clear

that the removal of Mg^{+2} and Ca^{+2} increased with the increasing contact time. Further, it also indicated that initially the metal ions adsorbed swiftly for a few minutes and subsequently reached at the equilibrium state. This result designates that due to the existence of greater number of active sites of Nps; rate of interaction between metal ions and $BaCO_3$ Nps is more. Afterwards, as the remaining vacant active sites decreases, the adsorption rate slow down due repulsive force between the same ions on both solid and liquid phase.
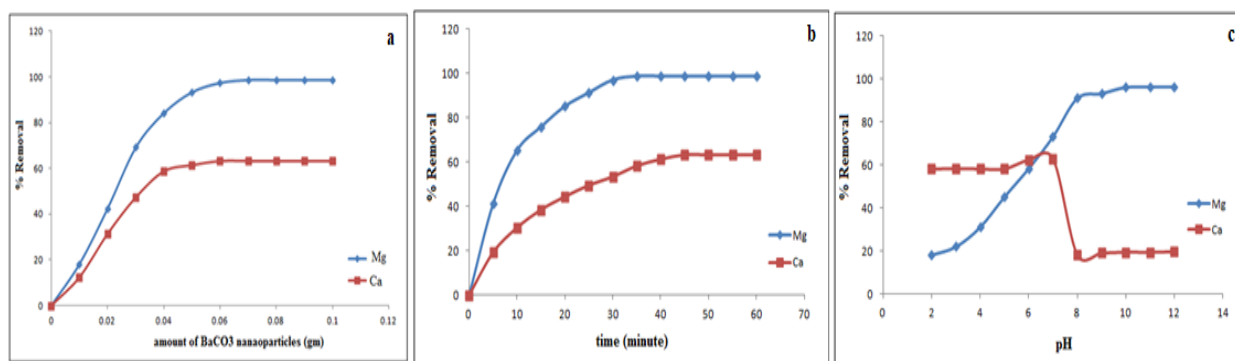
Fig.2 Effect of (a) dosage (b) time (c) pH on removal of hardness

Effect of pH

The pH of reaction environment influences on the removal of the metal ion solution and also on the properties of the $BaCO_3$ Nps. Fig.2(c) shows the removal of metal ions by Nps between pH range 2.0 to 12.0. It was observed that the percentage of removal for Mg^{+2} ions increased rapidly in basic pH environment it possibly due to formation of $Mg(OH)_2$. At higher pH, the surface of nanoparticles may acquire hydroxyl ions in alkaline media and the interactions of metal species with them are stronger than those with other functional groups. Further, Mg^{+2} are rapid reactive as compared to the Ca^{+2} ions; hence the %removal of Mg^{+2} ions increase with increasing pH. Moreover, removal of Ca^{+2} ions depend on the CO_3^{-2} species in solution, Ca^{+2} precipitated out as $CaCO_3$ after the interaction with CO_3^{-2}. In alkaline medium number of CO_3^{-2} species were less than ^-OH ions hence, % removal of Ca^{+2} were reduced at higher pH.

Effect of temperature

To estimate the effect of temperature on the removal of Mg^{+2} and Ca^{+2} from solution by $BaCO_3$Nps, we had selected the following temperatures: 298.15, 303.15, 313.15, 323.15, 333.15, 343.15 and 353.15K. In general, distribution co-efficient (K_D) is use to measure the efficiencies of various exchangers. The value of equilibrium distribution coefficient (K_D) was calculated using the following equation.

K_D= Cs/Cw(L/g)

Where, Cs is the concentration of Mg^{+2} and Ca^{+2} in the $BaCO_3$Nps (mg g-1) and Cw is Mg^{+2} and Ca^{+2} concentrations in aqueous solution (mg L^{-1}). The concentration of Mg^{+2} and Ca^{+2} in the $BaCO_3$Nps was calculated based on measurement of Mg^{+2} and Ca^{+2} in the water before and after the removal of Mg^{+2} and Ca^{+2} on the solid phase.

Fig.3 exemplifies the relationship between temperature and distribution coefficient (K_D).

It shows that the K_D values for both metal ions were very high and they increase with the reference of temperature. It signifies the endothermic ion exchange reactions of divalent cations which are favored by high temperatures (Fig.3).

The data of Mg^{+2} and Ca^{+2} removal at several temperatures have been used to evaluate the thermodynamic parameters of the system, according to the following equation:

$$ln K_D = \Delta S/R - \Delta H/RT$$
$$\Delta G = \Delta H - T\Delta S$$

where, K_D, ΔH, ΔS, R, T are distribution coefficients, enthalpy change, entropy change, ideal gas constant (8.3×10-3) kJK-1mol-1), and absolute temperature in Kelvin, respectively.

The enthalpy calculated from slope and entropy changes were calculated the intercept of van't Hoff plots ($ln K_D$ vs. 1/T). For Mg^{+2} values of ΔH and ΔS were 24.19 $kJmol^{-1}$ and 0.24 $kJmol^{-1}K^{-1}$ respectively. For Ca^{+2} values of ΔH and ΔS were 11.53 $kJmol^{-1}$ and 0.16 $kJmol^{-1}K^{-1}$ respectively.

The positive values obtained for ΔH and ΔS designate that the adsorption process is an endothermic and spontaneous. Further the result of ΔH value is between 8–20 $kJmol^{-1}$ indicated that removal process is governed by ion exchange [20]. The value for the process of the present research is between these ranges; therefore, it could be the evidence that ion exchange is the mechanism.

Ion-exchange isotherms

The degree of adsorption process can be estimated by adsorption isotherms. They provide a quantitative relationship between the adsorb equilibrium concentration of adsorbate, and also imitate the mechanism of the adsorption process. Here we apply analytical data in Langmuir and Freundlich isotherm models to investigate the adsorption process.
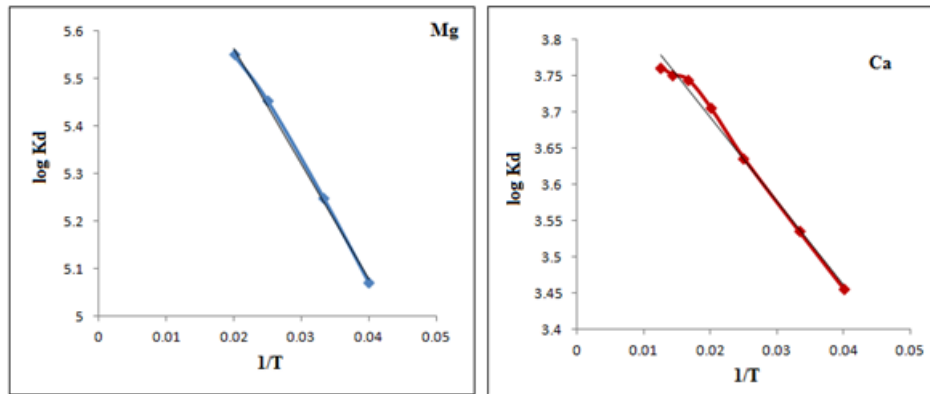
Fig.3 Effect of temperature on hardness removal

The Freundlich isotherm model is expressed as:

$$\log qe = \log K_f + 1/n \log Ce$$

where, qe is the adsorbed Mg^{+2} and Ca^{+2} ions at equilibrium per unit mass of $BaCO_3$Nps (mg g-1), constants, K_f and $1/n$ were minimum sorption capacity (mg g^{-1}) and adsorption intensity respectively. Ce is the equilibrium concentration of Mg^{+2} and Ca^{+2} ions.

Fig. 4 a,b shows a plot of log qe versus log Ce. The constants $1/n$ and $\log K_f$ values are obtained from the slope and intercept respectively. It is found that the related correlation coefficient R^2 value for the Freundlich model is 0.9466 for Mg^{+2} and 0.9404 for and Ca^{+2} ions.

The Langmuir isotherm is expressed as:

$$1/qe = 1/qobCe + 1/qo$$

where, qo is the maximum amount of the Mg^{+2} and Ca^{+2} ions per weight of $BaCO_3$ Nps to form the complete monolayer on the surface, Ce represent equilibrium concentration of adsorbate, qe is the amount adsorbate per unit mass of adsorbent, and b is the binding energy constant.

The linear plot of 1/Ce versus 1/qe (Fig. 5 a,b) show the graphical view of Langmuir adsorption isotherm. The related correlation coefficient (R^2) value for the Langmuir model is 0.9478 and 0.9740 for Mg^{+2} and Ca^{+2} ions respectively.

In the present system, there are three possibility of Mg^{+2} and Ca^{+2} ions removal, i.e., adsorption, hydro-lyzation, and precipitation transformation. From the above results of isotherms it is confirm that the experimental data neither fit in Langmuir isotherm or Freundlich isotherm model. Hence, the hardness removal mechanism with reference of Mg^{+2} and Ca^{+2} ions is not carried out by a simple adsorption process.
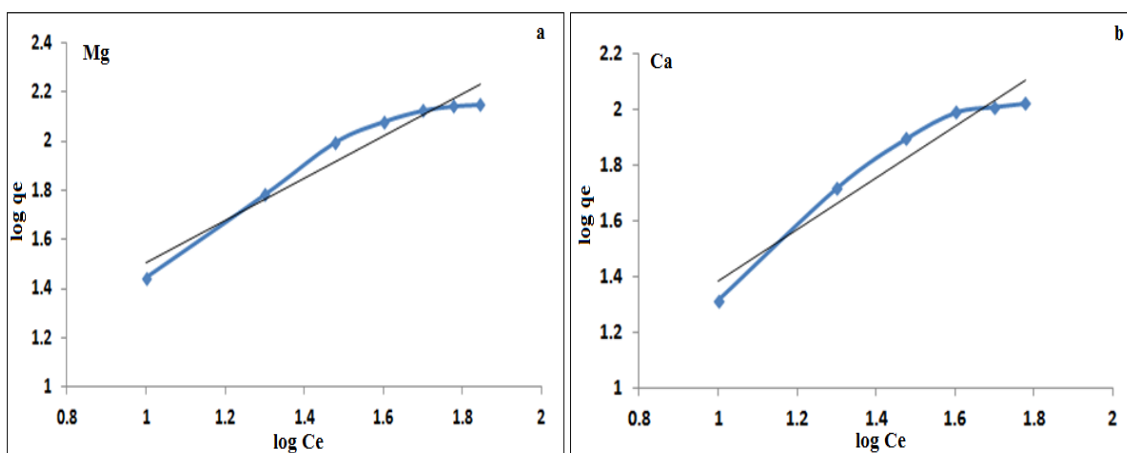

Fig.4. Freundlich isotherm model applied to the **(a)** Mg^{+2} **(b)** Ca^{+2} removal from aqueous solutions by $BaCO_3$ nanopartices

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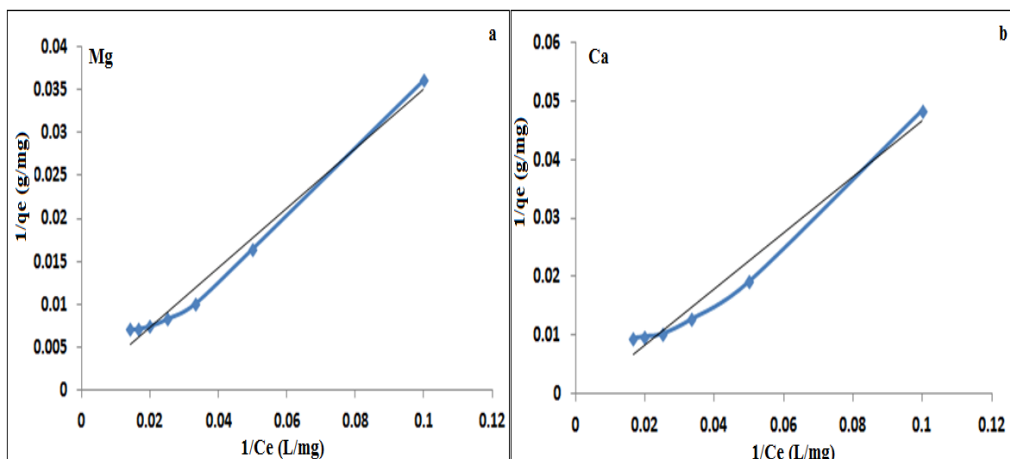Volume 04 Issue 13
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Fig.5. Langmuir isotherm model applied to the **(a)** Mg^{+2} **(b)** Ca^{+2} removal from aqueous solutions by $BaCO_3$ nanopartices

Furthermore, due to the existence of CO_3^{2-} ions precipitation transformation must be considered.

In addition, from the above study we observed that basic conditions are more effective for Mg^{+2} and Ca^{+2} ions removal. In such basic environment, metal ions could precipitate out into their respective hydroxide salts.

$$BaCO_3 + H_2O \rightarrow Ba(OH)_2 + CO_3^{-2}$$
$$Ba(OH)_2 + CO_3^{-2} + Mg^{+2} + Ca^{+2} \rightarrow Mg(OH)_2 + CaCO_3$$
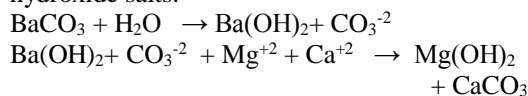
When $BaCO_3Nps$ added into the ionic solution (Mg^{+2} and Ca^{+2}), it is transformed into barium hydroxide immediately and the removal of Mg^{+2} and Ca^{+2} occurs by precipitation reaction. Here barium ions of barium hydroxide could exchange by Mg^{+2} ions rapidly as in comparison with to Ca^{+2} ions and form $Mg(OH)_2$, while on the other hand Ca^{+2} ions react with CO_3^{-2} ions and precipitate as $CaCO_3$.

Furthermore, in this process removal of Mg^{+2} is more than Ca^{+2} ions. This is due to the high aqueous solubility of Mg salt than Ca salts. In typical reaction of Ca-salts with $BaCO_3$ nanoparticles, Ca^{+2} ions replace barium ions and form $Ca(OH)_2$ and then react with CO_3^{2-} ions and form $CaCO_3$. In a mixture of Ca^{+2} and Mg^{+2}, Mg^{+2} ions preferentially interact with $BaCO3$ in compared to Ca^{+2} ions and further precipitate as $Mg(OH)_2$.

Analytical application

In Gujarat (India), there are many locations where water is hard due to the prescence of excess of dissolved solids than the acceptable limits (>600 mg L^{-1}) in ground water. The applicability of $BaCO_3$ nanoparticles in the field condition was tested with water samples taken from a pond of Kachchh, Peninsula of Saurashtra and from Narmada canal (Gandhinagar) Gujarat, India.

The nanoparticles reduced the level of hardness from collected samples using 0.070 g of $BaCO_3$ nanoparticle for 100 ml of sample within 30 min at room temperature (Table.2). Even though the nanoparticles were influenced by the presence of foreign cations, this factor did not affect lowering the Mg^{+2} and Ca^{+2} levels to the tolerance limit in field conditions.

Table 2 Real Application of BaCO3 nanoparticles for Mg^{+2} and Ca^{+2} removal

Sample	Initial Hardness (mg L^{-1})	Hardness after treatment (mg L^{-1})
Pond of Kachchh	1200	251
Peninsula of Saurashtra	950	190
Narmada canal	720	144

Conclusion

In conclusion, the barium carbonate nanoparticles were easily synthesized by a soft chemical method in a short time. A pure $BaCO_3$ phase (witherite) was obtained by this simple process. $BaCO_3$ Nps were applied for the removal of Mg^{+2} and Ca^{+2} ions. It was found that $BaCO_3Nps$ has become a powerful material for rapid removal of Mg^{+2} ions; it is also confirmed by various kinetic studies. Almost 98.8% Mg^{+2} ions were removed in 30 minutes. The kinetic studies also illustrate that the cations were removed by perception ion-exchange mechanism. Analysis of real samples shows that $BaCO_3Nps$ effectively

remove the initial hardness of water and improves the quality of water.

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