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Short communication

Application of eco-friendly method for nano-minerals preparation and ground water treatment

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ABSTRACT

This work aims at preparing different nano-minerals using bio-precipitation method (BPM). Nano-calcite (NC), nano-giorgiosite (NG), nano-witherite (NW) have been prepared by the addition of plant-derived urease enzyme (PDUE) to urea/$CaCl_2$, urea/$Ca(CH_3COO)_2$, urea/$MgCl_2$ and urea/$BaCl_2$ solutions, respectively. Nano-Mg-calcite (NMC) was precipitated by dissolving PDUE and urea in ground water (GW). Salt type plays an important role in the morphology, crystallinity, and particle size of nano-minerals. PDUE has higher effectiveness on Ca^{2+} removal from GW; meanwhile, it has a lower impact on Mg^{2+} removal. Where, the Ca-hardness varied from 1460 to 20 mg/l after the treatment of GW with PDUE. At the same pH, the Mg-hardness (1833 mg/l) slightly reduced to be 1210 mg/l. By raising pH, using one-molar sodium hydroxide solution, the removal of Mg2+ enhances. The BPM not only used to prepare innovative NMC-mineral from GW, but also applied to reduce GW-hardness.

1. Introduction

The formation of earth alkaline minerals has a great interest due to carbonates occur as the main mineral components in rocks and as inorganic components in exoskeletons and tissues of many mineralizing organisms (Pruss et al., 2010). Calcium carbonate ($CaCO_3$). is the most abundant mineral in nature (Render et al., 2016). The chemical precipitation of $CaCO_3$, magnesite ($MgCO_3$) and witherite ($BaCO_3$) polymorphs have been previously studied (Pochitalkina et al., 2016; Sun et al., 2015; Park et al. 2016).

Bio-precipitation of $CaCO_3$ and $MgCO_3$ is mainly carried out by urease active bacteria (usually *Sporosarcina Pasteurii*). Urease enzyme, secreted by bacteria, hydrolyzes urea {$(NH_2)_2CO$} to ammonium ions (NH_4^+) and dissolved inorganic carbon (CO_3^{2-}). The former increased the pH of the solution, and in the presence of Ca^{2+} or Mg^{2+}, the $CaCO_3$ or $MgCO_3$ has been precipitated (Abdel-Gawwad et al., 2016). There is no research works deal with the precipitation of $BaCO_3$ by bacteria, due to the inhibition impact of Ba^{2+} to bacteria, especially at high Ba^{2+} concentration (Sivolodskii, 2012). Calcite, magnesite and witherite are considered as important minerals with wide range of uses in several industries (Pruss et al., 2010; Sun et al., 2015; Lv et al. 2008). Calcium carbonate is widely used as extender in paint and filler in plastic. Magnesium carbonate is used in flooring, fireproofing and toothpaste. Barium carbonate is used in ceramic industry as gradient in glaze. The performance of these minerals can be enhanced, if they are used with nano-size.

This work deal with the application of bio-precipitation method (BPM) using plant derived urease enzyme (PDUE) to prepare different nano-minerals and reduce the ground water (GW) hardness by removal of Ca/Mg ions as nano-Ca/$MgCO_3$ precipitate.

2. Experimental

2.1. Materials

Jack bean meal urease was purchased from Oxford Laboratory Reagent Company, India. According to company certificate, 1 g of urease can hydrolyze 3 g of urea. Calcium chloride di-hydrate ($CaCl_2{\cdot}2H_2O$), calcium acetate {$Ca(CH_3COO)_2$}, magnesium chloride hexa-hydrate ($MgCl_2{\cdot}6H_2O$), barium chloride ($BaCl_2$), urea {$(NH_2)_2CO$), ethylene di-amine tetra acetic acid ($C10H_{16}N_2O_8$), murexide ($C_8H_8N_6O_6$) and Eriochrome black T ($C_{20}H_{12}N_3O_7SNa$) with purity of 99.99% were obtained from Fisher scientific chemical company, UK. GW was supplied from El-Wasta City, Beni-Suif Governorate, Egypt. The complexometric titration (ASTM D511, 2014) proved that the Ca^{2+} and Mg^{2+} concentrations in GW were 583 and 440 mg l^{-1}, respectively and

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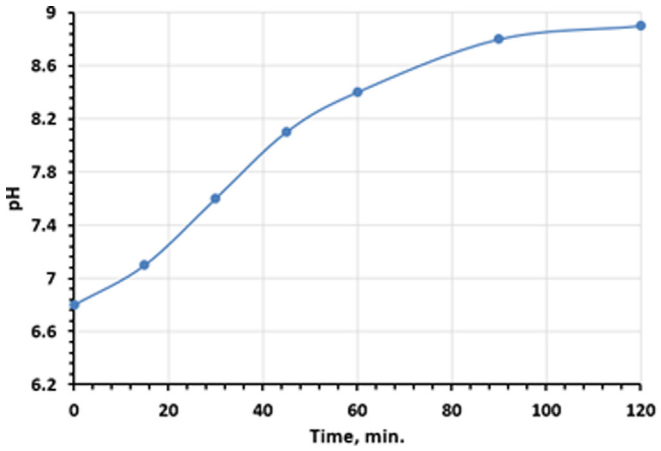

Fig. 1. pH development during urea hydrolysis by plant derived urease enzyme.

pH was 7.1. Fig. 1 showed the pH development with time of PDUE/urea solution. The pH increased with time, proving the fact that the PDUE hydrolyzes urea to produce CO_3^{2-} and NH_3^-, the later increased the pH of the solution.

2.2. Nano-minerals preparation

Nano-minerals preparation process was implemented by dissolving 10 g of plant derived urease enzyme (PDUE) in one liter of distilled water. A weight equivalent to 0.5 equimolar (M) of urea/$CaCl_2$, urea/$Ca(CH_3COO)_2$, urea/$MgCl_2$ and urea/$BaCl_2$ individually dissolved in PDUE solution. For Ca/Mg ions removal, 0.66 g/l of PDUE and 1.98 g/l of urea (equivalent to the concentration of Ca and Mg ions in GW) were dissolved in 100 ml of GW. All solutions were incubated for 2 h at 23 ± 2 °C. As pH-measurements, the pH of all solutions containing different salts changed from 6.7 at the beginning to 7.9 after 2 h of precipitation process. The pH of PDUE/urea-GW solution was 7.1; after 2 h, it raised to 7.4. After complete minerals precipitation process, the solid precipitates were washed several times by distilled water to remove any organic (urease) or inorganic (ammonium chloride) contaminants, then put in an oven at 80 °C for 3 h for drying. The dry precipitate was pulverized for 10 s by automatic grinder.

2.3. Instrumental techniques

The finely powder was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). For scanning electron microscopy (SEM), thin films of different minerals were prepared by the precipitation of these minerals on glass slides.

The crystals morphology of bio-precipitated minerals was investigated using SEM and the elemental compositions were identified by an energy dispersive X-ray analyzer (EDXRA). The mineralogical composition of precipitated minerals was characterized by XRD according to International Center for Diffraction Data (ICDD, 1991). The XRD-analysis was recorded on a Philips PW 1050/70 Diffractometer using a Cu-Kα source with a post sample Kα filter. The average crystallite size was estimated from the broadening of XRD-peaks (Scherrer, 1918). The actual particle size of minerals has been identified by TEM (JEM-HR-2001, Japan) with accelerating voltage of 200 kv. The purity of the prepared nano-minerals was measured by X-ray fluorescence (XIOS PW1400).

3. Results and discussion

Different minerals have been deposited when plant derived urease enzyme (PDUE) individually mixed with urea/$CaCl_2$, urea/$Ca(CH_3COO)_2$, urea/$MgCl_2$, urea/$BaCl_2$ and urea/GW solutions. These minerals presented different morphologies, depending on solutions compositions, as proved by SEM and EDRXA (Fig. 2a, b). Rhombohedral and fiber calcite crystals (where, polycrystalline fibers seem to be originate from central core) have been precipitated PDUE-urea/$CaCl_2$. When $Ca(CH_3COO)_2$ was used rather than $CaCl_2$, spherical calcite crystals being formed. The addition of PDUE to urea/$MgCl_2$ and urea/$BaCl_2$ solutions led to form hydrated magnesium carbonate with rod-like clusters crystals and needle-like witherite crystals, respectively. Distorted spherical Mg-calcite {Ca/Mg $(CO_3)_2$} crystals have been generated in case of PDUE-urea/GW system.

The preparation of different nano-minerals was performed according to the following equations:

$$MCl_2 + (NH_2)_2CO + 2H_2O \xrightarrow{PDUE} MCO_3 \downarrow + 2NH_4Cl$$

where, M is Ca, Mg or Ba cations.

In same manner, the removal of calcium and magnesium in GW was carried out as follows:

$$Ca/MgX + (NH_2)_2CO \xrightarrow{PDUE} Mg/CaCO_3 \downarrow + 2NH_4X$$

where, X is Cl or SO_4 anions.

The crystallinity as well as the average particle size of alkaline earth carbonates minerals were identified by XRD {Fig. 3}. The XRD proved that the calcite formed in case of PDUE-urea/$CaCl_2$ has higher crystallinity compared to that precipitated in case of PDUE-urea/$Ca(CH_3COO)_2$ system. Witherite and Mg-calcite minerals with low crystallinity have been observed in case of PDUE-urea/$BaCl_2$, and PDUE-urea/GW systems, respectively. Among all minerals giorgiosite {$Mg_5(CO_3)_4$. $(OH)_2{\cdot}5H_2O$}, precipitated in case of PDUE-urea/$MgCl_2$, showed the lowest crystallinity (tends to amorphous structure). The peaks positions are in good agreement with those for calcite, witherite, giorgiosite and Mg-calcite minerals powder obtained from the ICDD (1991). The average crystallate size of nano-minerals can be calculated from the broadening of minerals peaks using *Scherrer method* (Scherrer, 1918) as follows:

$$d = \lambda K/B\cos\theta$$

where, d is the average crystallate size, λ the diffraction wavelength (1.54 Å), K constant (0.94), B the full width at half maximum (FWHM) and θ is the diffraction angle. According to *Scherrer equation*, the average crystallate size of calcite deposited in case of PDUE-urea/$CaCl_2$ and PDUE-urea/$Ca(CH_3COO)_2$ were 20 and 9 nm, respectively. Giorgiosite, witherite and Mg-calcite minerals showed the average crystallate size of 11, 33 and 10 nm, respectively.

The estimation of particle size of nano-materials using Scherrer equation has two major limitations. The first is the value of the k constant changes with particles shape; the second includes the presence of defects in the crystalline lattice (Scherrer, 1918; Klug and Alexander 1974). So, other techniques, which defining the accurate particles size, should be applied.