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# **ORIGINAL ARTICLE**

# Plant extract-strategy using *Teucrium Polium* stems to green synthesize Ag/AgCl bionanocomposite imprinted on $Fe_3O_4$ /kaolinite and potentials in catalytic and chemosensor applications



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# **KEYWORDS**

*Teucrium Polium*; Bionanocomposite; Hg<sup>2+</sup> detection; 4-nitrophenol reduction; Separable catalyst **Abstract** A two-component bionanocomposite was produced with an easy and green method and was expanded to the three and four-component nanostructures. In fact, the Ag/AgCl sample with the mean diameter of about 22 nm was biosynthesized using the aqueous extract of *Teucrium Polium* and then it was imprinted on kaolinite to produce the Ag/AgCl/kaolinite bionanocomposite with a particle size range of 5–35 nm. For the first time, the four-component Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/ kaolinite bionanocomposite, composed of the 19 nm nanorods of Fe<sub>3</sub>O<sub>4</sub> in the vicinity of the 29 nm Ag/AgCl nanospheres was synthesized with the same method to promote the properties and applications. All the products could be utilized in the aqueous media, as both the useful biosensors to detect of Hg<sup>2+</sup> with a minimum concentration of 100  $\mu$ M and the efficient catalysts for the reduction of 4-nitrophenol to 4-aminophenol in 10–50 min. It's remarkable that the as-prepared composites were characterized using the various techniques such as UV-Vis, FT-IR, XRD, FE-SEM, and EDX. Further, the vibrating sample magnetometry (VSM) measurement revealed

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1878-5352 © 2022 The Authors. Published by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/). the ferromagnetic nature of  $Ag/AgCl/Fe_3O_4/kaolinite$ . Therefore, the four-component nanocomposite has the ability to separate easily with the aid of an external magnet, in addition to its other valuable advantages like easy work-up, and high catalytic efficiency and sensor performance. © 2022 The Authors. Published by Elsevier B.V. on behalf of King Saud University. This is an open access

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### 1. Introduction

With the rapid development of science and technology, heavy metals have been widely used at the industrial scale, which has an important function in the advancement of the human life. Nevertheless, their exceeding utilization has created serious threat for the environment and human health (Vilpan et al., 2005; Hong et al., 2011; Bilal et al., 2018). Among all the heavy metals, mercury compounds are widely used in various biological and industrial activates. Basically mercury is toxic in both elementary and combined form. Mercury in ionic form is extremely poisonous, accumulates in the environment with different transmitting channels such as water, food, and air and causes major harm to human organs (Lin et al., 2014; Weiss, 2007; Clarkson et al., 1981). This ion can penetrate from the skin and induce brain and kidney damages (Chakraborty, 2017; Larsen et al., 2018; Grandjean et al., 1998; Nolan and Lippard, 2008). The mercury poisoning results contain cardiac arrhythmias, stomach disorder, kidneys failure, hepatic enzyme disturbances, nose bleeding and blistering of the skin if present in the human body more than 5  $\mu$ gL<sup>-1</sup> (Hoyle and Handy, 2005; Langford and Ferner, 1999). Thus, a series of techniques including physical adsorption, biodegradation, potodegradation, and electrocatalysis have been used to eliminate the environmental contaminants. Among them, degradation with nanoparticles has become an effective method due to its great efficiency, mild reaction conditions, and environmental adaptability.

In most cases, the chemical synthetic methods of metal nanoparticles are not ecofriendly because of the physicochemical processes of reduction including hazardous chemicals, organic solvents, reducing agents, stabilizers, and capping agents (Shamaila et al., 2016). Additionally, the synthesized nanoparticles are expensive and contact with them or discharge them into the environment without treatment can make side effects for humans, beings and the environment (Rashtbari et al., 2020). Based on the previous studies, the green synthesis provides development, due to its low-cost, ecofriendly, and size-controlled, no waste energy and heat advantages, or not using toxic materials (Rashtbari et al., 2020; Duran et al., 2011; Seidi et al., 2022). Hence, the new strategies with biomaterials from the different sources have been gained attention. Among the bioactive materials, the plant extracts are of special interest because of their easier usage, less expense, and greater safe for the human applications (Kumar and Yadav, 2009; Sneha et al., 2010; Ghoreishi and Behpour, 2011; Taghizadeh and Rad-Moghadam, 2018). To date, many studies have focused on the synthesis of green nanostructures with the aid of plant extracts, but their application as sensor to detection and elimination of water pollutants, particularly the cations of transition metals, the consequence of industries, has rarely been reported (Rabiee et al., 2022; Devadiga, 2017; Uddin et al., 2017; Oluwafemi et al., 2019). The plants can create stable nanoparticles with long-term storage and without any aggregation (Jayaprakash et al., 2014). The minerals, proteins, organic acids, phenolics, and enzymes present in the structure of plants including the many reducing, oxidizing, capping, and stabilizing components, could improve the synthesis of nanoparticles (Liu et al., 2011). The mechanisms of metal resistance in the plants include binding to the cell-wall and chelating by metallothioneins, phytochelatins and the other metal binding proteins (Iravani, 2011; Hall, 2002). It has been suggested that polyols such as polysaccharides participate in the bio-reduction and stabilization of the metal ions to their

zero-valent forms according to researches on the possible mechanisms of metal reduction in the extracts. In return, the few researchers believe that the main reducing and capping agents are water soluble organics and protein (Sathshkumar et al., 2009). It has been studied that during the plant extract-based synthesis, the redox reactions are mediated by the presence of antioxidants, mainly. Recently, silver nanoparticle and its compounds especially the silver halides were extensively applied for the various area of science consist of medical, diseases diagnostics, catalysis, sensors, and etc (Parit, 2020; Song and Shi, 2019). Biological reduction in aqueous solution of silver ions (Ag<sup>+</sup>) produces Ag<sup>0</sup>, but also the AgCl nanoparticles which are the most common substances present in the ultimate product of biosynthesis of silver nanoparticles (Sharma et al., 2009; Duran et al., 2016). Also to further develop recyclable catalysts. the magnetic nanostructures have attracted a great attention (Xu et al., 2014; Adyani and Soleimani, 2019). Recently, the Fe<sub>3</sub>O<sub>4</sub> nanoparticles have been coated by various materials like surfactants, polymers, silica, cellulose and carbon to form a stable core-shell structure (Li et al., 2013; Liang and Zhu, 2016; Banazadeh et al., 2015; Vaddula et al., 2012; Yao et al., 2016; Li et al., 2014; Azari et al., 2021). Downloading such nanoparticles on natural supports not only prevents their aggregation during the catalytic progresses, but also provides an easy separation of them from the reaction mixture and reusing of them. The resulting heterogeneous catalyst has several benefits in comparison with their homogenous counterpart like easier work-up, better stability and reusability (Sheldon et al., 2000; Khalilzadeh et al., 2019). The clays are from the best naturally available solid supports because of their basal spacing, cation exchange capacity, the type of impurities, biocompability and resource renewability. Kaolinite is a hydrated aluminum silicate from a group of the natural kaolinite-serpentine clays in which the basic unit is 1:1 type layer consist of one continues network of tetrahedral sheet with Si4+ central atoms and one octahedral sheet with  $Al^{3+}$  central atoms. The sheets are held together by hydrogen band between the oxygen's in one of the alumina octahedral bond whereas the oxygen's are in one layer and the hydroxyl group are in the next layer. Hydrogen bonding between the adjacent layers prevents expansion of kaolinite (Feriancova et al., 2019).

In this project we used the aqueous extract of Teucrium Polium as a stabilizing and reducing agent for the green synthesis of Ag/AgCl nanoparticles. In order to fabrication of bionanocomposite, we utilized the kaolinite and magnetite as the other two components, a naturally solid support for the stabilization of metal nanoparticles and a ferromagnetic compound for magnetization of the synthesized nanocomposite. Further, the as-made new magnetic bionanocomposite (denoted as Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/kaolinite) was investigated for nakedeve sensing of Hg(II) ion. Moreover, these nanostructures could effectively catalyze the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) and decreases the toxicity of 4-NP from the natural waters. It's remarkable that 4-NP and its derivatives can pollute the natural water and wastewater systems especially green plants and aquatic organisms in the surface of the waters because of their high solubility, stability and toxicity (Sugiyama et al., 2012; San et al., 2002). Hence, an efficient treatment of wastewater containing 4-NP is very important and essential before its discharge into the aquatic environment. Moreover, the as-synthesized magnetic heterogeneous catalyst does not require filtration for the separation after the reaction completion, where it can be isolated with an external magnet easily and reused consecutively (Lu et al., 2007).

#### 2. Materials and methods

## 2.1. Materials

Analytical grade metal salts, (Hg(NO<sub>3</sub>)<sub>2</sub>, AgNO<sub>3</sub>, MgCl<sub>2</sub>·6H<sub>2</sub>-O, CuCl<sub>2</sub>, MnCl<sub>2</sub>·4H<sub>2</sub>O, CdCl<sub>2</sub>·H<sub>2</sub>O, ZnCl<sub>2</sub>, CoCl<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, VOSO<sub>4</sub>·5H<sub>2</sub>O, FeSO<sub>4</sub>·7H<sub>2</sub>O, Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·12H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub> and UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), commercial kaolinite, 4nitrophenol, sodium borohydride, absolute ethanol and ammonia solution (25%) were all purchased from Merck and were used without further purification.

# 2.2. Preparation of aqueous extract

The aqueous extract of *Teucrium Polium* was prepared using the freshly collected stems obtained in the city of Yasouj, Iran. Firstly, the stems were washed with distilled water for removing dust. Then, they were dried for 10 days in the shade at ambient temperature and were powdered. The resulting fine powder (0.1 g) was placed into an Erlenmeyer flask and was boiled with 10 ml of distilled water for 10 min. Finally, the solution was cooled down to ambient temperature, filtered, and kept at 4 °C for further use (Meva et al., 2016).

# 2.3. Preparation of nanostructures

**Ag/AgCl:** An appropriate volume of the extract  $(25, 50, 100 \ \mu$ l) was added to the 5 ml of 1, 2, 3, and 4 mM aqueous AgNO<sub>3</sub> solution and was incubated at 20 and 60 °C. In fact, a number of reaction conditions such as AgNO<sub>3</sub> concentration, the volume ratio of extract to AgNO<sub>3</sub> solution, temperature, and presence of light, were tested in a series of the optimizing

Table 1	All	the	experimental	conditions	for	the	synthesis	of
Ag@AgC	. 1.							

Sample	Concentration of AgNO <sub>3</sub> (mM)	Volume ratio of extract/AgNO <sub>3</sub>	Temperature (°C)
$S_1$	1	1/50	20
$S_2$	1	1/100	
S <sub>3</sub>	1	1/200	
$S_4$	2	1/50	
<b>S</b> <sub>5</sub>	2	1/100	
S <sub>6</sub>	2	1/200	
<b>S</b> <sub>7</sub>	3	1/50	
S <sub>8</sub>	3	1/100	
S <sub>9</sub>	3	1/200	
S <sub>10</sub>	4	1/50	
S <sub>11</sub>	4	1/100	
S <sub>12</sub>	4	1/200	
S <sub>13</sub>	1	1/50	60
S <sub>14</sub>	1	1/100	
S <sub>15</sub>	1	1/200	
S <sub>16</sub>	2	1/50	
S <sub>17</sub>	2	1/100	
S <sub>18</sub>	2	1/200	
S <sub>19</sub>	3	1/50	
S <sub>20</sub>	3	1/100	
S <sub>21</sub>	3	1/200	
S <sub>22</sub>	4	1/50	
S <sub>23</sub>	4	1/100	
S <sub>24</sub>	4	1/200	

experiments. Table 1 summarizes all the experimental conditions. The color change to brown indicated the synthesis of nanostructures that was monitored by the UV-Vis spectroscopy using the 1 cm quartz cells. For this purpose, the reference spectrum of the solvent (distilled water) was subtracted from that of the colloidal solution of the Ag/AgCl, and the data were collected from 300 to 800 nm with the 1 nm steps.

Ag/AgCl/kaolinite: For this purpose, kaolinite with the mass ratio of 1:1 was added to the 50 ml of 4 mM aqueous AgNO<sub>3</sub> solution and then was, stirred for 1 day. Then, 1000  $\mu$ l of the extract was added and incubated at 60 °C in front of the light for 24 h, as the optimizing conditions. On the other words, the Ag/AgCl nanoparticles were deposited onto the kaolinite by using this method. The color change to brown indicated the production of the Ag/AgCl/kaolinite bionanocomposite.

Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/kaolinite: The four-component nanocomposite was prepared through a three-step process. First, the Fe<sub>3</sub>O<sub>4</sub>/kaolinite with the mass ratio of 1:1 was synthesized by a hydrothermal method on the basis of our former procedure (Mansournia and Azizi, 2015). Kaolinite (0.122 g) was added to a solution of the FeSO<sub>4</sub>·7H<sub>2</sub>O (0.279 g) in 10 ml distilled water and was sonicated for 30 min. The beaker containing the resulting suspension together with another beaker containing 10 ml of the ammonia solution 25% were transferred into a stainless steel autoclave heated in an oven at 75 °C for 1 h. The Fe<sub>3</sub>O<sub>4</sub>/kaolinite product was obtained after centrifugation and washing with distilled water and the absolute ethanol for several times, followed by drying at 70 °C. In the second step, the as-prepared Fe<sub>3</sub>O<sub>4</sub>/kaolinite was added to the 50 ml aqueous AgNO<sub>3</sub> solution (4 mM) and then was, then, stirred for 1 day. In the final step, 1000 µl of the extract was added to this solution and was incubated at 60 °C in front of the light for 24 h to reduce the  $Ag^+$  ions to  $Ag^0$  on the Fe<sub>3</sub>O<sub>4</sub>/kaolinite surface. After the obtained brown suspensions cooled down to the room temperature, they were centrifuged, and the products were washed with distilled water for several times and dried at 60 °C for 12 h. Scheme 1 briefly illustrates the preparation of Ag/AgCl/ Fe<sub>3</sub>O<sub>4</sub>/kaolinite bionanocomposite.

# 2.4. Instruments

The chemical bonding features of the synthesized Ag/AgCl, Ag/AgCl/kaolinite, and Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/kaolinite nanocomposites were studied on the dry powders by a magna 550 FT-IR instrument in the range of 4000–400 cm<sup>-1</sup> using the KBr pellets. All of the as-made bionanocomposites were characterized by powder X-Ray Diffraction (XRD) patterns on a Philips X'Pert Pro X-ray diffractometer equipped with Nifiltered Cu K $\alpha$  source at a scan range of 10 < 2 $\theta$  < 80. The field emission scanning electron microscope (FE-SEM, MIRA3 TESCAN) were applied to found the morphology and size of the bionanocomposites, followed by the investigation of the particle size distribution via estimating the diameter of 50 particles on the magnified SEM images using the Digimizer software. The elemental composition was performed using the Energy Dispersive X-Ray Spectroscopy (EDX, SAMX). The vibrating sample magnetometry (VSM) measurements were carried out at room temperature by a Meghnatis Daghigh Kavir Co. instrument.



Scheme 1 Briefly illustration of the preparation process of Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/kaolinite bionanocomposite.

#### 2.5. Detection experiments

The potential of the as-synthesized bionanocomposites for the detection of mercury (II) cation was evaluated as follow: an aqueous solution of Hg(NO<sub>3</sub>)<sub>2</sub> with appropriate concentration was added to the aqueous suspension of the bionanocomposite. Then, the change in the absorption spectrum of the resulting solution (2 ml) in the presence of different concentrations of the Hg<sup>2+</sup> (1–300  $\mu$ M) was studied through the UV-Vis technique. Further, the selectivity of the as-prepared bionanocomposites for the Hg<sup>2+</sup> detection was investigated via the stock solutions (400  $\mu$ M in distilled water) of various metal ions (Hg<sup>2+</sup>, Ag<sup>+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>, Mn<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Vo<sup>2+</sup>, Fe<sup>2+</sup>, Cr<sup>3+</sup>, Pb<sup>2+</sup>, and UO<sub>2</sub><sup>2+</sup>). Furthermore, the absorption intensity change of the synthesized nanocomposites suspensions containing an especial concentration of the Hg<sup>2+</sup> in the presence of the 400  $\mu$ M of a metal ion from the other cations was studied.

## 2.6. Catalytic experiments

The catalytic performances of the prepared nanocomposites were tested by carrying out the reduction of 4-NP to 4-AP at room temperature using the aqueous solution of NaBH<sub>4</sub> as a reducing agent. Typically, 0.17 mg of nanocomposites and 1.0 ml of freshly prepared NaBH<sub>4</sub> solution (1.5 M) were sequentially added to 10 ml of the 4-NP solution (120  $\mu$ M) under magnetic stirring at room temperature (Zheng et al., 2015). The progress of the reaction was monitored by the UV-Vis spectroscopy.

# 3. Results and discussion

#### 3.1. Characterizations

**UV-Vis Spectroscopy:** The formation of the Ag/AgCl, Ag/AgCl/kaolinite, and Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/kaolinite samples in the presence of the *Teucrium Polium* extract was followed by

UV-Vis technique. The absorbance of the aqueous reaction mixtures was scanned from 300 to 800 nm. The Surface Plasmon Resonance (SPR) feature at ca. 400-460 nm was typical for the Ag nanoparticles covered on the surface of the AgCl. It should be noted that the color of the as-synthesized product had to be reddish to dark brown (Shu et al., 2014; Meva et al., 2016). The appearance of the metallic Ag on the surface of the AgCl nanostructures is the reason for the conversion of the AgNO<sub>3</sub> solution to the brown suspension, and the color of the Ag/AgCl/kaolinite and Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/kaolinite changed to cloudy dark brown because of the presence of kaolinite. In reality, the as-introduced biological method was used under different conditions listed in Table 1, to have greater control of stability and size. As can be seen in Fig. 1a, the intensity of SPR peak is increased with enhancement in volume ratio of extract/AgNO<sub>3</sub> from 1/200 (S<sub>24</sub>) to 1/100 (S<sub>23</sub>) and 1/50 $(S_{22})$ , AgNO<sub>3</sub> concentration from 1 mM  $(S_{13})$  to 4 mM  $(S_{22})$ and temperature from 20 °C (S<sub>10</sub>) to 60 °C (S<sub>22</sub>). According to these investigations the efficiency was maximal in the extract/AgNO<sub>3</sub> volume ratio of 1/50 and AgNO<sub>3</sub> concentration of 4 mM and 60 °C (S<sub>22</sub>). Under this optimization, the browning of the AgNO<sub>3</sub> solution was completed 24 h after the addition of the aqueous extract; the similar conditions were created for the biosynthesis of all three nanocomposites. Moreover, the stability of the as-synthesized Ag/AgCl nanocomposites could be observed in Fig. 1b, that with increasing the synthesis time from 24 h to 48 h, 66 h, 4 days, 7 days, and then 11 days, the slight changes in the spectrum are observed. The optical absorption spectra of the products, the Ag/AgCl, Ag/AgCl/kaolinite, and Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/kaolinite, are shown in Fig. 1c. Thus, it could be argued that the metabolites present in the extract, such as alkaloids, flavonoids, and saponins, acted as the reducing groups and converted the silver ions  $(Ag^{+})$  to  $Ag^{0}$  nanoparticles (Gawali and Jadhav, 2018).

**FT-IR Spectroscopy:** The FT-IR analysis was performed before and after the bioreduction process to recognize the possible interaction between the molecules of the extract, AgNO<sub>3</sub>, kaolinite, and Fe<sub>3</sub>O<sub>4</sub>. In the FT-IR analysis of the *Teucrium Polium* stems extract (Fig. 2a), the strong absorption at



Fig. 1 UV-Vis absorption spectra of the Ag/AgCl suspensions in the various conditions (a), different times (b), and those of three bionanocomposites in optimized condition (c).

approximately 3420 cm<sup>-1</sup> corresponded to the hydrogen bonded O-H stretching vibrations of alcohol moieties that was weaken in the related spectrum following the bioreduction to Ag/AgCl (Fig. 2b). Moreover, the band at 1614 cm<sup>-1</sup>, which was bioreduced to 1623 cm<sup>-1</sup> in the related nanocomposites, corresponded to the C = O asymmetric stretching vibration. It's remarkable that these two vibrations of extract were weaken in the FT-IR spectrum of Ag/AgCl, but not disappeared. It means that the nanoparticles exist as coated by a thin layer of the phytochemicals derived from the extract. In the spectrum of the Ag/AgCl/kaolinite (Fig. 2c), two bands observed near 3695 and 3620 cm<sup>-1</sup> can be assigned to the stretching vibrations of the external and the internal hydroxyl groups of kaolinite, respectively. Furthermore, the broad absorptions centered at about 3430 and 1630 cm<sup>-1</sup> in both spectra of Ag/AgCl/kaolinite (Fig. 2c) and Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/ kaolinite (Fig. 2d) are ascribed to the stretching and bending vibrational modes of the adsorbed water molecules on the surface of the nanocomposites. The absorption bands at about 1110, 1030 and 1007 cm<sup>-1</sup> are assigned to Si-O stretching vibrations, Si-O stretching in the muscovite and quartz interference, respectively. Moreover, the vibrational modes at around 915 cm<sup>-1</sup> and 792 cm<sup>-1</sup> indicated the inner surface Al-OH deformation. The bands assigned to Si-O (quartz interference), Si-O-Al stretching, and Si-O-Si bending of kaolinite molecules are seen at about 696, 540, and 470 cm<sup>-1</sup>, respectively (Hoor et al., 2020; Olusegun and Mohallem, 2020). Generally, the prominent sharp band at 1380–1383 cm<sup>-1</sup> seemed to be assigned to the vibrations of methyl groups. The absorption observed at ca. 2922 cm<sup>-1</sup> is due to C-H asymmetric stretching



**Fig. 2** FT-IR spectral analysis before and after bioreduction: dried *Teucrium Polium* extract (a), and the as-made Ag/AgCl (b), Ag/AgCl/Kaolinite (c) and Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/Kaolinite (d).

vibration of CH<sub>2</sub> group. According to the presence of some bands related to the functional groups of the extract in the spectra of bionocomposites, it can be said that the extract has played an important role in the stabilization of the asmade Ag/AgCl, Ag/AgCl/kaolinite, and Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/ kaolinite nanocomposites in the aqueous medium. On the other hand, the FT-IR analysis exhibited that the reduction of silver ions to form stable silver nanoparticles may be affected by the coordination behaviors between hydroxyl functional groups of the biomolecules and the amino groups in the dried extract.

**XRD Analysis:** The powder XRD analysis was performed to estimate the crystal constructional phase of the as-made nanocomposites. In the XRD plot of the Ag/AgCl bio-nanocomposite (Fig. 3a), the diffraction lines with 20 amounts of 38.37, 44.53, 64.70, and 77.64 corresponded to the planes 111, 200, 220, and 311 of the cubic Ag, respectively (JCPDS card No. 01-087-0717). Additionally, the reflections at 28.03,



Fig. 3 XRD patterns of Ag/AgCl (a), Ag/AgCl/Kaolinite (b) and Ag/AgCl/Fe $_3O_4/Kaolinite$  (c).

32.46, 46.46, 55.08, and 57.71, indicated, respectively, the lattice planes 111, 200, 220, 311, and 222 of the cubic phase of the AgCl crystal, all in accordance with JCPDS card No. 01-085-1355.

As can be seen in Fig. 3b, with respect to the Ag/AgCl/kaolinite nanocomposite, the Bragg's reflections with 20 values of 38.32, 44.40, and 64.53 were assigned to the crystal planes of 111, 200, and 220, respectively, which could be readily attributed to the standard cubic Ag phase, in accordance with JCPDS card No. 01-087-0717. The diffraction peaks of the nanocomposite at  $2\theta = 27.81$ , 32.32, 46.23, and 55.35 could be ascribed to the Miller indices 111, 200, 220, and 311 of the cubic phase AgCl crystal, matching JCPDS card No. 01-085-1355. Moreover, the defined hollow spheres were in good agreement with the kaolinite (JCDPS No. 00-005-0143), along with small amounts of quartz where the two intense peaks at 12.44° and 24.98°, as the characteristics of kaolinite, corresponded to the planes 001 and 002, respectively (Mahloujifar and Mansournia, 2019). Further, Fig. 3c presents the XRD pattern of the magnetic Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/kaolinite sample in the range of 10-80°. The peaks appeared at  $2\theta = 30.37, 35.73, 43.36, 57.42, and 63.00$  could be indexed to 220, 311, 400, 511, and 440 planes, respectively, in accordance with the standard XRD data for the inverse spinel cubic crystal structure of Fe<sub>3</sub>O<sub>4</sub> (JCPDS card No. 01-076-1849). The other diffraction lines in this pattern were also related to the Ag, AgCl, and kaolinite components as mentioned above.

The successful synthesis of the four-component bionanocomposite and its crystallinity were demonstrated by the sharpness and intensity of the reflection lines (Wang et al., 2010). The average crystallite sizes of the Ag, AgCl, and Fe<sub>3</sub>O<sub>4</sub> were calculated on the basis of the planes 111-Ag, 200-AgCl, and 311-Fe<sub>3</sub>O<sub>4</sub>, respectively, using the Scherrer relation (Eq. (1)) (Jenkins and Snyder, 1996):

$$D = 0.9\lambda/\beta cos\theta_B \tag{1}$$

In this formula,  $\lambda$ ,  $\beta$ , and  $\theta_B$  are the X-ray wavelength, full width at half the maximum (FWHM), and Bragg diffraction angle of the XRD peak, respectively. The estimated crystallite size (D) of the Ag and AgCl were 28.2 and 34.6 nm for the Ag/AgCl and 15.0 and 37.1 nm for the Ag/AgCl/kaolinite. Likewise the crystallite size of the Ag, AgCl, and Fe<sub>3</sub>O<sub>4</sub> nanostructures in the as-made magnetic Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/kaolinite bionanocomposite were estimated as about 47.0, 46.2, and 32.8 nm, respectively.

FE-SEM Analysis: The field emission scanning electron microscopy revealed the aggregated Ag/AgCl nanoparticles, as depicted by the size distribution histogram in Fig. 4a with the mean diameter of about 22 nm. The FE-SEM image of the as-synthesized Ag/AgCl/kaolinite bionanocomposite (Fig. 4b) illustrated the sphere-like Ag/AgCl nanoparticles deposited on the surface of the kaolinite sheets. Kaolinite featured a smooth and regular surface without impurities, which could significantly promote the assembly of the Ag/AgCl nanoparticles. Moreover, the size distribution histogram revealed a narrow distribution of the particle size (5-35 nm) and the mean diameter of about 19 nm, consistent with the average crystallite size estimated from the XRD data. Also, Fig. 4(c, d) show the nanorods of the  $Fe_3O_4$  with the average diameter of about 19 nm, in the vicinity of the Ag/AgCl nanospheres with the average size of 29 nm, on the surface of the



Fig. 4 FE-SEM images of the as-synthesized bionanocomposites: Ag/AgCl (a), Ag/AgCl/Kaolinite (b),  $Ag/AgCl/Fe_3O_4/Kaolinite$  in two scales (c, d) with its size distribution histograms (insets) related to  $Fe_3O_4$  nanorods (c) and Ag/AgCl nanoparticles (d).

kaolinite sheets, in two scales of 200 and 500 nm. It's remarkable that the formation of the numerous pores on the irregular surface of the nanocomposites increases the surface area and facilitates the adsorption process (Mahdavinia et al., 2016).

**EDX spectroscopy:** The EDX spectroscopy was applied to check the elemental composition of the as-made nanocomposites based on the existence of silver, chlorine, aluminum, silicon, and iron. As observed in Fig. 5a, the Ag/AgCl sample contained silver and chlorine due to their characteristic optical absorption peaks detected at about 3 and 2.6 KeV, respectively. In the case of the Ag/AgCl/kaolinite bionanocomposite, the spectrum 5b confirmed the presence of noticeable amounts of silver, chlorine, aluminum, and silicon derived from the Ag/AgCl nanoparticles and kaolinite nanosheets, devoid of any impurities. The elemental composition results of the Ag/AgCl/kaolinite introduced Fe in addition to the previous elements present in Fig. 5b, according to the Fig. 5c.

**VSM measurement:** The VSM technique was employed to analyze the dynamic magnetic properties of the as-obtained  $Ag/AgCl/Fe_3O_4/kaolinite$  bionanocomposite. From the room temperature magnetization curve, illustrated in Fig. 5(d), the magnetic saturation, remanence, and coercivity were determined as 21.69 emu/g, 2.55 emu/g, and 50 Oe, respectively. The magnetic hysteresis of the Ag/AgCl/Fe\_3O\_4/kaolinite represented its magnetic behavior, so that the saturation magnetization demonstrated the superparamagnetic nature of the bionanocomposite. High loading portions of the Fe<sub>3</sub>O<sub>4</sub> nanorods is the reason for the high saturation magnetization of the Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/kaolinite bionanocomposite that contributed to the high magnetic activities along with the superparamagnetic performance. Moreover, The Fe<sub>3</sub>O<sub>4</sub> nanocrystallites could be coordinated with the phytochemicals of the extract which has been affected on their superparamagnetic behavior (Toorchi Roudsari et al., 2019). Further, due to the superparamagnetic property, the produced nanocomposite exhibited a fast response to an external magnetic field and was quickly separated from the reaction mixture (Chen et al., 2014; Laurent et al., 2008). The reversible process is an advantage in many applications, thus the preparation of the superparamagnetic nanocomposites using nontoxic biological resources has a potential application in many fields such as pharmaceuticals and medicine for drug delivery systems, inducing MRI agents and hyperthermic effects in cells.

#### 3.2. Applications of bionanocomposites

Sensing performances: Different values of an aqueous solution of  $Hg^{2+}$  were added to the bionanocomposites in water (2 ml in PH = 7) to check the sensitivity and detection range evaluation of the as-prepared nanocomposites. The color changes of all the produced mixtures were monitored using photo-imaging and UV-Vis spectroscopy. Figs. 6–8a indicate the absorption spectra of the suspensions of the Ag/AgCl, Ag/AgCl/kaolinite, and Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/kaolinite nanocomposites, following the



Fig. 5 EDX spectra of Ag/AgCl (a), Ag/AgCl/Kaolinite (b), Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/Kaolinite (c) and the room temperature magnetization curve of the as-made Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/Kaolinite bionanocomposite (d). The inset shows the magnetic hysteresis loop at lower applied fields.

addition of mercury(II) in the concentration range of 1–300  $\mu$ M. Another important property of the bionanocomposites designed as the chemosensor is their selectivity for the detection of Hg<sup>2+</sup> in the environmental water samples, where there are various metal ions in addition to Hg<sup>2+</sup> with relatively higher concentrations. Accordingly, the UV-Vis absorption spectra of the aqueous solution of nanocomposites in pH = 7 against 400  $\mu$ M of different metals (Hg<sup>2+</sup>, Ag<sup>+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>, Mn<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Vo<sup>2+</sup>, Fe<sup>2+</sup>, Cr<sup>3+</sup>, Pb<sup>2+</sup>, and UO<sub>2</sub><sup>2+</sup>) were compared, Figs. 6–8b. As noted, it appears that no metal ion could omit the related SPR band like Hg<sup>2+</sup>, suggesting the excellent selectivity of the as-made nanocomposites for the detection of Hg<sup>2+</sup>.

absorption spectra of the bionanocomposites in the presence of  $Hg^{2+}$  (150 µM for Ag/AgCl and Ag/AgCl/kaolinite, and 100 µM for Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/kaolinite) and 400 µM of other metal ions from the aforementioned cations have been showed in Figs. 6–8c. It is observable that the other metal ions had no remarkable effect on the detection of  $Hg^{2+}$ , and the color change of the suspensions was similar to that in the absence of the second metal ions because they were not able to oxidize silver nanoparticles. As noted in these figures, in the absence of  $Hg^{2+}$ , the characteristic SPR bands of the Ag/AgCl, Ag/AgCl/ kaolinite, and Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/kaolinite nanocomposites occurred at 416, 419, and 450 nm, respectively. On the other hand, with the increasing of the  $Hg^{2+}$  and disappearance of



**Fig. 6** UV-Vis spectral change of aqueous Ag/AgCl suspension; (a) after addition of  $Hg^{2+}$  in different concentrations (1–300  $\mu$ M), (b) after addition of 400  $\mu$ M of various metals, and (c) in the presence of 150  $\mu$ M  $Hg^{2+}$  and 400  $\mu$ M of another metal ion, and (d) plot of absorbance at 418 nm versus concentration of  $Hg^{2+}$  (1–200  $\mu$ M).

the brown color of the solution, the absorbance band of the bionanocomposites decreased in intensity, hence revealing a shift to lower wavelengths. The absorbance values at the aforementioned wavelengths depended on the dispersed amounts of the samples, decreasing by degradation via the redox reaction between  $Ag^0$  and  $Hg^{+2}$  in the outer layer of the bionanocomposites on the basis of the Equation (2).

$$Hg^{2+}_{(aq)} + Ag_{(nano)} \to Hg^{0}_{(s)} + Ag_{(nano)} + Ag^{+}_{(aq)}$$
 (2)

The standard electrode potentials of the  $Ag^+/Ag$  and  $Hg^{2+}/Hg$  were 0.799 V and 0.855 V, respectively. The redox reaction between  $Ag^0$  and  $Hg^{2+}$  was not very fast because of

the small difference between their standard electrode potentials. It is, nevertheless, well established that the physical and chemical properties of the nanoparticles differ from those of bulk case due to the size quantization. Therefore, the effective difference between the  $Ag^+/Ag_{(nano)}$  and  $Hg^{2+}/Hg$  would be much higher, leading to the reduction of  $Hg^{2+}$  to  $Hg^0$  with the partial oxidation of the  $Ag^0$ . Further, due to a high affinity between the  $Ag^0$  and  $Hg^0$ , the reduced form of mercury ( $Hg^0$ ) was deposited on the Ag surfaces, resulting in the formation of the Ag/Hg alloy. This phenomenon reduced the SPR intensity of the Ag/AgCl, Ag/AgCl/kaolinite, and  $Ag/AgCl/Fe_3O_4/$ kaolinite nanocomposites associated with the small red shift



**Fig. 7** UV-Vis spectral change of aqueous Ag/AgCl/Kaolinite suspension; (a) after addition of  $Hg^{2+}$  in different concentrations (1–300  $\mu$ M), (b) after addition of 400  $\mu$ M of various metals, and (c) in the presence of 150  $\mu$ M Hg<sup>2+</sup> and 400  $\mu$ M of another metal ion, and (d) plot of absorbance at 419 nm versus concentration of  $Hg^{2+}$  (1–200  $\mu$ M).

(Rastogi et al., 2014; Narayanan and Han, 2017). Further, Fig. 9(a-c) indicate the color change (from brown to colorless) of the Ag/AgCl, Ag/AgCl/kaolinite, and Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/ kaolinite suspensions following the addition of mercury (II) in the concentration range of 1–300  $\mu$ M. According to these findings, it could be emphasized that the Ag/AgCl, Ag/AgCl/ kaolinite, and Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/kaolinite bionanocomposites, green synthesized by the extract of *Teucrium Polium* stems, could offer great sensitivity for the detection of Hg<sup>2+</sup>. By comparing the spectra in Figs. 6–8(a-c), it can be concluded that the Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/kaolinite bionanocomposite is the most efficient sensor for detection of mercury(II), so that the lower concentration of  $Hg^{2+}$  (Fig. 8c, 100  $\mu$ M instead of 150  $\mu$ M) in the presence of other cations was applied in order to evaluate the selectivity of this bionanocomposite. In total, it seems that the magnetic four-component product is a better suggestion for sensor application than the Ag/AgCl and Ag/AgCl/kaolinite nanocomposites.

It is one of the crucial mandates, that a sensing element should provide linearity between its input variable and the output variable for any inference or the measurement application. According to the Figs. 6–8d, an excellent linearity was found between concentrations of Hg(II) range from 1  $\mu$ M to 200  $\mu$ M with the negative slope indicating a decrease in absor-



**Fig. 8** UV-Vis spectral change of aqueous Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/Kaolinite suspension; (a) after addition of Hg<sup>2+</sup> in different concentrations (1–300  $\mu$ M), (b) after addition of 400  $\mu$ M of various metals, and (c) in the presence of 100  $\mu$ M Hg<sup>2+</sup> and 400  $\mu$ M of another metal ion, and (d) plot of absorbance at 440 nm versus concentration of Hg<sup>2+</sup> (1–200  $\mu$ M).

bance with increase in Hg2 + content. Moreover the limit of detection (LOD) was found by using the below Equation:

$$LOD = 3\sigma/b \tag{3}$$

Where  $\sigma$  and b are the standard deviation and slope of the calibration curve, respectively. The LOD of the Ag/AgCl, Ag/AgCl/Kaolinite, and Ag/AgCl/Fe3O4/Kaolinite nanocomposites was calculated to be 15.25, 15.35, and 15.27  $\mu$ M. These LOD values is better than those of several other Ag nanoparticles probes in Table 2. This result indicates the ability of these sensing to efficiently analyze aqueous samples quantitatively up to low micro-molar level.

**Catalytic performances:** Three bionanocomposites were examined for the catalytic reduction of the 4-NP in the aqueous media using NaBH<sub>4</sub> as a reducing reagent. After the addition of NaBH<sub>4</sub>, the maximum absorption band of the 4-NP changed from 317 nm to 400 nm due to the production of the 4-nitrophenolate ions in the alkaline condition, following the color change from light yellow to bright yellow. As depicted in Fig. 10, the peak at 400 nm disappeared, accompanied by the appearance of a peak at 300 nm, demonstrating the reduction of the 4-NP to 4-AP. As also indicated in Fig. 10(a-c), in the presence of the Ag/AgCl, Ag/AgCl/kaolinite, and

 Table 2
 Comparative studies on sensing and catalytic applications of the reported Ag nanoparticles and nanocomposites with the present study.

Nanostructure	Synthetic method	Size	Hg <sup>2+</sup> sensing performance	Catalytic performance	Ref.
Ag nanoparticles	<i>Terminalia</i> <i>catappa</i> leaves extracts	11 nm	12.75–0.85 $\mu$ g/ml HgCl <sub>2</sub>	-	(Devadiga, 2017)
Ag nanoparticles	Garlic extract	9– 35 nm	$0-90 \ \mu gLOD = 2 \ \mu M$	_	(Ghosh et al., 2018)
Ag nanoparticles	<i>Matricaria recutita</i> extract	11 nm	$5-15 \text{ ppmLOD} = 25 \mu \text{M}$	_	(Uddin et al., 2017)
Ag nanoparticles	<i>hyacinth</i> plant leaves extract	10.5 nm	0.01–100 µM	_	(Oluwafemi et al., 2019)
Ag nanoparticles	<i>G. resinifera</i> plant extract	13– 44 nm	-	20 min	(Parit, 2020)
Ag/Fe <sub>2</sub> O <sub>3</sub> nanocomposites	hydrothermal and solvothermal	16– 40 nm	-	5-120 min	(Wang et al., 2020)
Ag/rGO nanocomposites combined with S. oneidensis MR-1	Chemical	3– 10 nm	-	10-20 min	(Song and Shi, 2019)
$CeO_2/g-C_3N_4/Ag$ nanocomposite	<i>Piper betle</i> leaves extract	-	-	10 min	(Pinheiro et al., 2019)
Ag/AgCl, Ag/AgCl/Kaolinite and Ag/AgCl/	Teucrium Polium	5–	1–	10-50 min	This work
Fe <sub>3</sub> O <sub>4</sub> /Kaolinite nanocomposites	extract	35 nm	$300 \ \mu MLOD = 15.3 \ \mu M$		



Fig. 9 Visual observations of color change in the aqueous suspensions of Ag/AgCl (a), Ag/AgCl/Kaolinite (b), and Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/Kaolinite (c) in the presence of different concentrations of  $Hg^{2+}$ .

 $Ag/AgCl/Fe_3O_4$ /kaolinite bionanocomposites, the solution became colorless after 10, 50, and 25 min, respectively.

It is necessary to mention that the peak at 400 nm was not altered even after 48 h in the absence of bionanocomposites, emphasizing that NaBH<sub>4</sub> alone could not possibly reduce 4-NP. Thus, it seems that the catalytic performances of the nanocomposites in the reduction of 4-NP were due to the transfer of electron and the hydrogen atom from BH<sub>4</sub><sup>-</sup> to this organic compound (Sun et al., 2013; Lin and Doong, 2011). The catalyst may facilitate the charge transfer during the reduction process as an effective electron relay system. In fact, the reactant molecules uptake on the surface of the catalyst, and the reduction performs through a six-electron transferring process from  $BH_4^-$  to 4-NP. On the other hand, the positively charged surface of the kaolinite mediated the reaction between the two negatively charged species of BH4 and 4nitrophenolate anions. Therefore, the reaction could be summarized in three steps: (1) adsorption of the reactant on the catalyst surface, (2) reduction of the 4-NP with transferring of electrons from  $BH_4^-$  to nitrophenolate anions both adsorbed on the surface, and (3) desorption of the 4-AP. The presence of the electrons on the surface of the catalyst also help with the uptake of electrons by 4-nitrophenolate anions and, thereby, its reduction to 4-AP (Kong et al., 2017).

Based on the reduction catalytic activity of these nanocomposites, the rate constant was calculated using the following Equation:

$$Ln(A/A_0) = -kt \tag{4}$$

Where  $A_0$  and A are the initial absorbance of solution and its absorbance at appropriate time of reduction reaction, respectively, at the related  $\lambda_{max}$  of the deprotonated 4-NP (400 nm), and k is the rate constant of the reaction, which could be calculated from the fitted kinetic curves of ln (A/  $A_0$ ) versus time (Wang et al., 2020). From Equation 4, the reduction activity can be considered to be as pseudo-first-



Fig. 10 UV-Vis spectral change of 4-NP solution after addition of  $NaBH_4$  in the presence of Ag/AgCl (a), Ag/AgCl/Kaolinite (b), and Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/Kaolinite (c) in different times, and the rate constants (k) for 4-NP reduction using the different nanocomposites (d).

order type. As can be seen in Fig. 10(d), the k values of the Ag/AgCl, Ag/AgCl/kaolinite, and Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/kaolinite bionanocomposites were 0.651, 0.481, and 0.607 min<sup>-1</sup>, respectively. So it seems that, among catalysts above, the Ag/AgCl and Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/kaolinite nanocomposites are more efficient catalysts for the reduction of 4-NP to 4-AP.

By comparing the results of our study and similar recent researches on the applications of the green synthetic Ag nanostructures, listed at Table 2, it can concluded that the present work has good achievements. Further, the as-made bionanocomposites have been applied for both mercury (II) sensing and catalytic reduction of 4-NP, while other studies have been reported the use of their synthesized nanoparticles in only one of these areas.

#### 4. Conclusions

In this study, we synthesized the Ag/AgCl and Ag/AgCl/Kaolinite nanocomposites with the particle size of about 22 and 19 nm, respectively, in a green, fast and economical manner using the extract of Teucrium Polium stems. Also, we successfully synthesized a magnetic separable and heterogeneous catalyst and high-quality chemosensor, the Ag/AgCl/Fe<sub>3</sub>O<sub>4</sub>/kaolinite bionanocomposite, using the same extract for the first time. The crystalline nature and the optical, morphological and elemental aspects, and magnetometry measurments of the as-made nanocomposites were characterized by the XRD, UV-Vis, FE-SEM, EDX, and VSM techniques. The results of the FT-IR analysis revealed that the plant biomolecules could play a role in the reduction of Ag<sup>+</sup> into stable silver nanoparticles. The products used as sensitive and selective sensors for the detection of  $Hg^{2+}$  (150  $\mu M$ for Ag/AgCl and Ag/AgCl/kaolinite, and 100 µM for Ag/AgCl/  $Fe_3O_4$ /kaolinite) in the presence of different metal ions (400  $\mu$ M) in the aqueous media. Further, they could catalyze the reduction of 4-NP to 4-AP by NaBH<sub>4</sub> between 10 and 50 min. According to the results, the Ag/AgCl nanocomposites could be the most efficient catalysts with the reduction time of 10 min. Moreover, the magnetic Ag/ AgCl/Fe<sub>3</sub>O<sub>4</sub>/kaolinite sample which demonstrated better sensing application for detection of  $Hg^{2+}$  than other synthetic bionanocomposites, can exhibit a fast response to an external magnetic field and is quickly separated from the reaction mixture due to the superparamagnetic property.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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