Fabrication of Poly (Meth Acrylamide)-Chitosan Nanoparticles Graft Copolymer Using Potassium Chromate/Mandelic Acid Redox Pair for Waste Water Treatment

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Accepted: 26 March 2022 / Published online: 19 April 2022
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Abstract
Unreported graft copolymer of Meth Acrylamide (MAam) and our previously prepared and fully characterized chitosan nanoparticles (CNPs) as a starting substrate has been synthesized under nitrogen atmosphere using potassium chromate / mandelic acid as unique redox pair. This was done to see the impact of both CNPs with respect to well-dispersed nano sized particles, large surface areas, biodegradability and reactivity, MAam as highly reactive nitrogen containing monomer and the aforementioned novel redox pair with respect to a notable reduction in polymerization temperature for enhancing the graft yield %. The effect of reaction conditions on the graft yield % has been deliberated with respect to CNPs, MAam, potassium chromate, mandelic and sulphuric acids concentration in addition to polymerization time and temperature. The resultant copolymer has been characterized by FTIR spectroscopy and thermo gravimetric analysis. The results obtained reflect the following findings for the resultant copolymers in comparison with CNPs counterpart; (a) higher thermal stability (b) higher graft yield % obtained when [CNPs] 1.0 g, [potassium chromate] 100 mmol/l, [Mandeic acid], 80 mmol/l, [suphuric acid], 100 mmol/l, [MAam], 150% bows, reaction time, 120 min., and reaction temperature, 45 °C were used, (c) higher mercury ions scavenging activity and % removal when different dosage and extent of grafting of the copolymer are used up to the level required for industrial application, (d) recovered by washing the mercury ions from the complex with weak acid 1 N HNO₃ (pH 2) and its metal-binding activity was slightly bargain by this process, and (e) a preliminary mechanism representing all occasions that occur during the polymerization reaction has been projected.

Keywords Chitosan nanoparticles · Potassium chromate · Meth acrylamide · Graft copolymerization · Redox pair

Introduction
It is well known recently that a great effort in different laboratory word-wide has been focused on the fabrication of low molecular weight chitosan in such a way to increase its potential applications in different disciplines [1–6]. For this purpose, chitosan, a distinct biodegradable well-known natural carbohydrate polymer, is an excellent candidate for the production of nano-sized chitosan nanoparticles in the range of (1–100 nm) that exhibit distinct properties and effective process parameters due to the large number of particles and high surface area to volume ratio, magnetic separation, surface chemistry, and surface interactions, as well as the relatively high water solubility in comparison to other polymers [7]. In this regard, and to primarily augment their potential applications, particularly for waste water remediation via heavy metal ions and dyes sorption, the graft copolymerization process with highly reactive hydrophilic monomers, as one of the most fascinating fields for chemical modification of polysaccharides without affecting their bulk characteristics, serves as the most efficient process currently being used [8–10]. Chitosan nanoparticles comprise two types of reactive functional groups that can be grafted: (i) free amine groups and (ii) hydroxyl groups. As a result, several functional groups have been grafted onto the backbone of chitosan nanoparticles, imparting changed properties. Several studies on graft copolymerization of chitosan nanoparticles with classical free radical initiators such as ferrous ammonium sulphate, ceric ammonium nitrate, potassium persulphate, and ammonium persulphate have been conducted to persuade desired functionalities [11–14]. The characteristics of graft
copolymers are determined by a variety of factors, including molecular structure, side chain, number, and length [15, 16]. Whereas the primary challenge for scientists worldwide when using traditional free radical graft copolymerization methods is the lack of commercial synthesis methods, lower graft yield percent, uncontrolled formation of homopolymer, and low reproducibility, in addition to high energy, temperature, water, and chemical consumption [17–19]. Keeping the foregoing in mind, and in order to avoid the latter shortcomings of traditional free radical initiators, a redox initiation system may be employed to commence the graft copolymerization reaction, which is dependent on free radicals produced during the oxidation–reduction reaction. The relative lower activation and energy savings of redox initiators can result in radical generation at realistic rates throughout a very wide temperature range, including initiation at moderate temperatures of 0–50 °C and even below [18, 20–25]. As a result, our laboratory’s research team concentrated on in-depth basic research on structural modifications of inexpensive, naturally occurring, biodegradable, nano-sized lower surface area, and highly reactive chitosan nanoparticles as non-fibrous textile via graft copolymerization using potassium chromate in presence of mandelic acid as an energy saving novel redox pair for initiating grafting as the first target. Furthermore, as the second target, meth acrylamide is used as a reactive hydrophilic nitrogen-containing monomer with regard to its availability, hydrophilicity, and efficacy, which imparts many smart properties onto the resulting copolymer via the addition of a new functionality to CNPs. As a third aim, the application of the resulting copolymer with varied graft yield percent and dosages for mercury ion removal from aqueous solution was also investigated. This was accomplished by assessing the primary factors influencing the graft copolymerization process in terms of CNPs, MAam, potassium chromate, mandelic, and sulphuric acid concentrations, as well as polymerization duration and temperature. The characteristics of the generated copolymer were carefully studied utilizing multiple world-class facilities such as FTIR and TGA. To the best of our knowledge, the aforementioned method for copolymer production, namely based on chitosan nanoparticles and the aforementioned utilized redox pair, has never been published in the literature (a point that has not been reported in the literature).

Experimental

Materials

Chitosan nanoparticles with sizes ranging from 60 to 100 nm were prepared as a starting substrate using a polymerization procedure that embraces the consecutive addition of native chitosan to a dilute solution of meth acrylic acid, resulting in the polymer suspended on a nano scale via polymerizing MAA in chitosan solution. Unless otherwise indicated, a known weight of chitosan (0.8 g) was dissolved in an aqueous meth acrylic acid solution (0.5%, wt/v) for 24 h under magnetic stirring to homogenize. The aforementioned solution was then treated with 0.02 mol/l potassium permanganate as an initiator for 2 h at 60 °C, resulting in the creation of CNPs, which were subsequently cooled in an ice bath. The suspension was centrifuged at 6000 rpm for 45 min, and the supernatant was collected. The settling CNPs from the centrifugation process were then freeze-dried. The so-obtained chitosan nanoparticles with 10–15% yield has been fully characterized using SEM, TEM, FTIR, XRD, TGA and particle size analyzer according to the work published by [5]. Meth Acrylamide (E. Merck) was recrystallized using benzene/methanol mixture and dried in vacuum. Potassium chromate (Sigma–Aldrich, USA), Malonic acid (E. Merck, India), acetic acid (E. Merck, India) and sulfuric acid (Sigma–Aldrich, USA) were used as such and all the solutions were prepared in double distilled water. Throughout the tests, analar grade ethyl and methyl alcohols were employed. Hg(CH₂CO₂)₂ was a compound of analytical reagent grade that was utilized without additional purification.

Procedure for Grafting

Chitosan nanoparticles solution was generated for each experiment by dissolving it in acetic acid, as described in the literature [26]. The reactor was filled with a determined amount of chitosan nanoparticles (0.25–2.0 g), MAam (25–150% based on weight of substrate), sulphuric acid (10–100 mmol/l), and mandelic acid (10–100 mmol/l), and a steady stream of oxygen-free nitrogen gas was fed through for 30 min at a constant temperature. To start the reaction, a specified quantity of potassium chromate solution (10–100 mmol/l) was added. The process was carried out in the presence of a constant supply of oxygen-free nitrogen gas. The flask content was kept in a thermostatic water bath at different temperatures (35–50 °C) for different time interval (15–180 min). By taking the above in mind, the order of adding ingredients was kept constant in all the performed experiments. After the desired reaction time, the grafted chitosan samples were separated by neutralizing excess acetic acid with a dilute sodium hydroxide solution, filtered, and washed with distilled water until pH 7 was reached. The sample was then pressed between two filter sheets and dried in an electric oven at 60 °C for 4 h before being chilled overnight over P₂O₅ in a vacuum desiccator.

Homopolymer Removal

At the end of the reaction, the contents of the flask were poured over 100 ml of ethyl alcohol, where a precipitate of poly (MAam)–chitosan nanoparticles graft copolymer and poly (MAam) (homopolymer). The latter can be entirely
removed by washing with a 50:50 mixture of ethyl alcohol and water at 50 °C numerous times (for 25 min each), filtering, and lastly drying in an electric oven at 65 °C for 5 h. It was discovered experimentally that washing 2–3 times with the aforesaid combination is sufficient for full homopolymer removal in physical mixtures of chitosan/poly (MAam) by monitoring the nitrogen content of these mixtures after each wash until it reached a consistent value. This is in total accord with the results reported by other researchers [5, 27] for complete homopolymer removal.

N. B.

Poly(MAam)–chitosan nanoparticles graft copolymers with variable graft yields were combined by keeping the grafting reaction conditions constant and varying just the quantity of MAam concentration.

**Metrological Precision Estimation of the Graft Yield (%) via Titrimetric Method**

The graft yield (%) was appraised titrimetrically by tracing the nitrogen % of the grafted sample via acid base titration and the graft yield (%) was calculated as follows:

\[
\text{GraftYield\%} = \frac{100(\text{N\%} \times 0.85)}{100 - (\text{N\%} \times 0.85)}
\]

where 0.85 is the molecular weight of meth acrylamide /100.

**Proof of Grafting via Instrumental Technique**

**Fourier Transforms Infrared Spectroscopy (FTIR)**

Fourier transform infrared (FTIR) spectroscopy was carried out using a Perkin Elmer Spectrum 2000 FTIR spectrometer under dry air at room temperature. About 4 mg of the copolymer powder was blended with 200 mg of potassium bromide and about 40 mg of the mixture was used to prepare a pellet.

**Thermo Gravimetric Analysis (TGA)**

Thermal gravimetric analysis TGA was carried out on Perkin–Elmer Pyris TGA in N2 atmosphere, temperature range of 40–600 °C, and heating rate of 10 °C/min.

**Mercury Ions Removal**

Unless otherwise specified, an aqueous solution of fixed concentration (Hg 208 ppm) of mercury ions was generated by dissolving 0.33 g mercuric acetate (Hg (CH3COO)2) in 1 L double distilled water. The dispersion of chitosan nanoparticles and poly (MAam)–chitosan nanoparticles graft copolymers (0.5–3.0 g) was then agitated for 15 min at room temperature to create a polymer mercury ion complex. The latter was subsequently separated by filtering, and the filtrate was utilized to analyze remaining metals with an atomic absorption spectrophotometer.

**Recovery of the Prepared Copolymer**

Poly (MAam)–chitosan nanoparticles graft copolymers with graft yields ranging from (17.3–50.2%) at pH 7 utilized to remove mercury ions; were redispersed in distilled water (40 ml), and the dispersion was adjusted to pH 2 by adding 1 N HNO3 solution. The dispersion was filtered after 10 min of stirring. The copolymer residue was washed with water, adjusted to pH 7 with 1 N NaOH, and dried overnight at 40 °C. The amount of Hg removed by the recovered copolymer was measured and compared to that of the unrecovered copolymer.

**Statistical Analysis and Metrological Precision**

All of the experiments were conducted in triplicate. The data were analyzed and expressed as mean values ± standard deviations and error bars with standard error. This was done to insure about the high precision of metrological measurements all over the work when using our calibrated instruments in our institute either by primary standard apparatus or certified reference materials used especially for this purpose.

**Results and Discussion**

**Determination of Optimum Grafting Reaction Conditions**

The graft copolymerization reaction was carried out at various reactant concentrations to evaluate their influence on the graft yield percent based on our laboratory trials and published papers in the last three decades [18, 22–25, 27] to acquire the optimum range explored. Potassium chromate (PC), mandelic acid (MA), meth acrylamide (MAam), chitosan nanoparticles (CNPs), sulphuric acid, and the temperature and time period of polymerization are the reactants.

**Potassium Chromate Concentration**

The impact of changing the potassium chromate concentration on the graft yield percent of poly (MAA)-chitosan nanoparticles graft copolymer has been investigated, and the findings are shown in Fig. 1a. The graft yield percent was shown to rise as the potassium chromate concentration was increased within the range examined, i.e. from 10 to 100 mmol/l. This might be because when the concentration of chromate ion increases, so does the concentration of active species, resulting in an increase in the concentration.
of primary free radicals and an increase in graft yield percent.

**Mandelic Acid Concentration**

Figure 1b depicts the findings obtained by varying the concentration of mandelic acid (MA) from 10 to 100 mmol/l. The graft yield percentage rose when the concentration of mandelic acid was raised from 20 to 80 mmol/l. This rise in graft yield percent is related to an increase in the quantity of primary free radical species production. A further rise in mandelic acid concentration over 80 mmol/l may result in the formation of a high number of free radical species, resulting in the premature end of the developing grafting chain and reduced grafting.

**Hydrogen Ion Concentration**

The impact of hydrogen concentration has been explored in Fig. 1c by increasing the concentration of sulphuric acid from 10 to 100 mmol/l. By raising the hydrogen ion concentration within the specified range, the graft yield percent was observed to rise. This is due to the fact that the concentration of $\text{H}_2\text{CrO}_4$ increases as the concentration of hydrogen ions increases, as stated in the following equation.

$\text{CrO}_4^{2-} + 2\text{H} \rightarrow \text{H}_2\text{CrO}_4$

As a result of the interaction of $\text{H}_2\text{CrO}_4$ with the mandelic acid molecules, more primary free radicals are produced, leading to an increase in graft yield percent.

**MAam Concentration**

Figure 1d denotes the effect of MAam concentration on graft yield % by varying its concentration from 25 to 150% based on weight of substrate (bows). Graft yield % was found to increase on increasing the concentration of MAam. The increase in graft yield % might be attributed due to accumulation of monomer molecules at the close proximity to the CNPs polymeric backbone. The monomer molecules, which are at immediate vicinity of reaction sites become acceptors of CNPs resulting in chain initiation and thereafter themselves becomes free radical donor to neighboring molecules causing the lowering of termination.

**Chitosan Nanoparticles Concentration**

To scrutinize the consequence of chitosan nanoparticles concentration on graft yield %, its concentration has been varied from 0.25 to 2.0 g. The graft yield % increase on increasing the concentration of chitosan nanoparticles up to 1, 0 g, but beyond this concentration range, graft yield % decrease (Fig. 1e). The increment in graft yield % up to certain concentration range could be explained due to the availability of more grafting sites with increasing concentration of chitosan nanoparticles, however on further increasing the concentration beyond 1.0 g, the viscosity of the medium increases, which hinders the movement of free radicals thereby decreasing the graft yield %.

**Effect of Time Period**

The influence of reaction time was investigated by varying the time intervals from 15 to 180 min (Fig. 1f). Graft yield percentage was observed to grow as reaction time rose up to 120 min, then decline. This trend may be explained by the fact that as the reaction develops and time passes, the amount of graft copolymer grows owing to the availability of more active species, resulting in a low proportion of homopolymer. However, after 120 min, the expanding grafted chain may terminate at a quicker pace, resulting in a decrease in grafting parameters.

**Effect of Temperature**

It has been found that graft yield % increases as temperature increases from 35 to 45 °C, but thereafter the values of graft yield % are found to decrease (Fig. 1g). The increase in
the values of the graft yield % may be attributed due to the fact that with increase in temperature, rate of production of primary free radicals increase, causing an increase in value of graft yield %. However, further, increase in temperature that is above 45°C, there is decrease in graft yield %, which might be due to destruction of primary free radicals due to effective collisions at higher temperature.

**Tentative Mechanism**

Free radical (R·) is generated by the interaction of potassium chromate ion and mandelic acid. They abstract hydrogen atom from CNPs and produce CNPs-O· and CNPs-NH· macro radicals respectively at the OH and NH2 sites of the CNPs molecule. The MAam molecules which are in close vicinity of the reaction sites become acceptor of chitosan nanoparticles radical resulting in chain initiation of graft copolymer and thereafter themselves become free radical donor to neighboring molecules. In this way grafted chain grows. These chains are terminated by coupling to give graft copolymer. The following tentative mechanism has been suggested for the graft copolymerization of MAA onto CNPs using potassium chromate/ mandelic acid redox pair.

**Primary Free Radical Species Formation**

\[
\text{H}_2\text{CrO}_4 + \text{C}_6\text{H}_5\text{CH(OH)COOH} + 4\text{H}^+ \rightarrow \text{Cr}^{4+} + \text{C}_6\text{H}_5\text{CH(OH)COOH} + 3\text{H}_2\text{O}
\]

\[
\text{Cr}^{4+} + \text{C}_6\text{H}_5\text{CH(OH)COOH} \rightarrow \text{C}_6\text{H}_5\text{C}(\text{OH})\text{COOH} + \text{H}^+ + \text{Cr}^{3+}
\]

(R·)

**Initiation**

\[\text{R}^- + \text{M} \rightarrow \text{RM}^-\]
\[\text{CNPs} - \text{OH} + \text{RM}^- \rightarrow \text{CNPs} - \text{O}^- + \text{RMH}\]
\[\text{CNPs} - \text{NH}_2 + \text{RM}^- \rightarrow \text{CNPs} - \text{NH}^- + \text{RMH}\]

**Propagation**

\[\text{CNPs} - \text{O}^- + \text{M} \rightarrow \text{CNPsM}^-_1\]
\[\text{CNPsM}^-_1 + \text{M} \rightarrow \text{CNPs} - \text{M}^-_2\]
\[\text{CNPsM}^-_n + \text{M} \rightarrow \text{CNPs} - \text{M}^-_n\]
\[\text{RM}^- + \text{M} \rightarrow \text{RM}^-_1\]

RM\(_1\) + M → RM\(_2\)
RM\(_{n-1}\) + M → RM\(_n\)

**Termination**

\[\text{CNPs} - \text{M}_n^- + \text{CNPs} - \text{M}^-_n \rightarrow \text{Ploy (MAA)} - \text{chitosan nanoparticles graft copolymer}\]
\[\text{CNPs} - \text{M}_n^- + \text{RM}^-_n \rightarrow \text{Ploy (MAA)} - \text{chitosan nanoparticles graft copolymer}\]
\[\text{RM}^-_n + \text{RM}^-_m \rightarrow \text{Homopolymer}\]

**Evidence of Grafting**

**Fourier Transform Infrared (FTIR) Spectroscopy**

The presence of the meth acrylamide functional groups in ploy (MAam)-chitosan nanoparticles graft copolymers was confirmed instrumentally by FT-IR spectra as shown in Fig. 2. Ploy meth acrylamide spectrum (Fig. 2a) parades a bands at 3379 cm\(^{-1}\) due to vibrational N–H group and other at 1648 cm\(^{-1}\) ascribing to the vibrational C=O group of the amide as a main functional groups of the monomer used. While, in case of chitosan nanoparticles spectrum (Fig. 2b), a primarily a broad absorption band around at 3290 cm\(^{-1}\) due to vibrational O–H and vibrational N–H is present. On the other hand, IR spectrum of poly(meth acrylamide)-chitosan nanoparticles graft copolymer (Fig. 2c) shows the presence of a band at 1693 cm\(^{-1}\) which could be assigned to the stretching vibration of amide carbonyl group which confirmed the grafting reaction of MAam onto CNPs backbone structure.

**Thermo Gravimetric Analysis (TGA)**

Figure 3 depicts the thermo grams of chitosan nanoparticles and ploy (MAam)-chitosan nanoparticles graft copolymer.
is seen Fig. 3 that, the initial weight loss for chitosan nanoparticles was about 10% and that of ploy (MAam)-chitosan nanoparticles graft copolymer was 1.0% at 100 °C, corresponding to the evaporation of intra and intermolecular moisture. At 200 °C, weight loss of about 14% for chitosan nanoparticles and 2.0% for ploy (MAam)-chitosan nanoparticles graft copolymer was detected, correlating to thermal breakdown of functional groups such as OH on the chitosan nanoparticles backbone structure. On the other hand, the weight loss of 34.0% and 55.8% for chitosan nanoparticles and 29.20% and 46.00% for ploy (MAam)-chitosan nanoparticles graft copolymer, respectively, were recorded at the temperature range between 300 and 400 °C. These results demonstrated that ploy (MAam)-chitosan nanoparticles graft copolymer is more thermally stable compared with chitosan

Fig. 2  FTIR spectrum of Poly Meth acrylamide (a), Chitosan nanoparticles (b), and Poly (meth acrylamide)-chitosan nanoparticles graft copolymer (c). Reaction conditions: Details of the conditions used are given in the text.
nanoparticles. The lower thermal stability of the latter may be due to the reduction in particles size (60–100 nm).

**Applications in Waste Water Treatment**

**Effect of Chitosan Nanoparticles Dosage**

Interestingly, it was vital here in our study to scrutinize the residual and % mercury ions removal of both chitosan nanoparticles as a starting substrate and poly (MAam)–chitosan nanoparticles graft copolymer having specific graft yield (i.e. 50.2) at neutral pH just for comparison. The residual mercury ions were assessed over different doses of chitosan nanoparticles and poly (MAam)–chitosan nanoparticles graft copolymer concentration ranged from 0.5 to 3.0 g. The obtained results are drawn in Fig. 4. When the dose of chitosan nanoparticles and poly (MAam)–chitosan nanoparticles graft copolymer derived thereof added to the mercury ions solution (208 ppm Hg) was increased from 0.5 to 3.0 g, the residual Hg content in the filtrate decreased gradually depending on the used dose (Fig. 4a). The results designate that the residual Hg content of chitosan nanoparticles and poly (MAam)–chitosan nanoparticles graft copolymer decreased with increasing concentration and leveled off at a
2.5 g sample concentration. The maximal residual mercury ion removal for both poly (MAam)–chitosan nanoparticles graft copolymer and chitosan nanoparticles were 70 and 120 ppm (representing 62.98 and 42.3.0% removal as shown in Fig. 4b), which reflect the superior mercury ions removal in case of poly (MAam)–chitosan nanoparticles graft copolymer smart material than native chitosan nanoparticles. This may be attributed to the introduction of an extra functional group (i.e. amide groups) onto chitosan nanoparticles backbone via grafting process using our novel redox pair potassium chromate/mandelic acid initiation system and MAam monomer. In addition to the saturation occurred at 2.5 g at which further increase in biopolymer dosage had little or no effect on mercury ions removal. This information should be relevant in determining the most cost-effective dosage of that biopolymer for copper ion elimination.

Extent of Grafting

Five levels of poly (MAam)–chitosan nanoparticles graft copolymers with varying degrees of grafting (17.3 to 50.2%) were utilized to estimate residual and percent removal of mercury ions from its solutions at 208 ppm concentration and pH 7 for 30 min. The obtained results are set out in Fig. 5. Details of the conditions used are set out elsewhere. It is seen from Fig. 5 that, increasing the extent of grafting of the copolymer from 17.3 to 50.2% would lead to a decrease in residual mercury ion concentration from 208 to 70 ppm at pH 7 representing 66.36% removal (Fig. 5b). This indicates that the mercury ions in the solution interact more likely with higher extent of grafting i.e. 50.2% with the introduced functional groups i.e. amide groups of poly (MAam)-chitosan nanoparticles graft copolymer, which reflect the role of extent or degree of grafting on the mercury ions binding activity or removal.

Recovery of Copolymer

Figure 6 shows the comparison between poly (MAam)-chitosan nanoparticles graft copolymer having different graft yields % before and after recovery using 1 N HNO3 (pH 2). Details of the conditions used are given in the text. It is seen from the figure that, the residual mercury ions removal efficiency of the recovered copolymer appears slightly less than that of fresh one unrecovered. In case of Hg removal, the recovered copolymer of 50.2% (pH7) reduced the mercury ion content to 99 ppm in comparison to 70 ppm for unrecovered one.
Conclusion

Chitosan nanoparticle as starting substrate was graft copolymerized with MAam using potassium chromate/mandelic acid as a novel redox pair. It was found that the graft yield % was high, when [CNPs] 1.0 g, [potassium chromate] 100 mmol/l, [Mandeic acid], 80 mmol/l, [sphuric acid], 100 mmol/l [MAam], 150% bows, reaction time, 120 min., and reaction temperature, 45 °C were used. The spectroscopic data and TGA analysis confirm the grafting of MAam onto CNPs, which is supported by a tentative mechanism suggested for grafting. The grafting of meth acrylamide chains enhanced the thermal stability of the resulting copolymers. Finally application of the resultant copolymers having different dosages and extent of grafting showed an increase in metal scavenging activity and % removal up to the level required for industrial application.

Acknowledgements The author wishes to thank the spirit of Prof M.A. Ramadan (NRC) for his valuable data and characterization tools in addition to our laboratory staff in NIS for the facilities provided either for helping and preparing chemical and instruments for analysis.

Funding Open access funding provided by The Science, Technology & Innovation Funding Authority (STDF) in cooperation with The Egyptian Knowledge Bank (EKB). The authors have not disclosed any funding.

Declarations

Conflict of interest There is no conflict of interest.

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