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ORIGINAL RESEARCH PAPER

Microwave-Assisted Synthesis of kappa-Carrageenan Beads Containing Silver Nanoparticles with Dye Adsorption and Antibacterial Properties

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ABSTRACT

In this work, we used a simple and totally green method for synthesizing silver nanoparticles using kappa-carrageenan as reducing and stabilizing agent. The beads were prepared in aqueous medium by microwave heating, and then followed by cross-linking with K^+ cations without using any additional toxic and expensive chemical agents. The preparation method of the carrageenan-based beads is easy, fast, simple, effective, and safe. The synthesized beads loaded with were characterized by ultraviolet-visible absorbance spectra, transmition electron microscopy and X-Ray diffraction techniques. The as-prepared beads were evaluated to remove cationic crystal violet dye from aqueous solutions. The thermodynamic parameters shown that the sorption process was feasible, spontaneous and endothermic. The kinetics and isotherm of crystal violet adsorption were found to well fit to pseudo-second-order kinetic and Langmuir isotherm model, respectively. Moreover, the antibacterial activity of the obtained beads was examined using the nutrient agar disc diffusion method.

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INTRODUCTION

In recent years, metal nanoparticles have been gained much attention because of their unique properties such as increased surface area to volume ratio and increased activity [1,2]. Among them, silver nanoparticles (AgNPs) have attracted numerous research interest due to improved antibacterial properties and their relatively nontoxicity to human cells [3-5]. There are many methods for the preparation of AgNPs. The chemical reduction of silver salt by using of a reducing agent is the most widely used method for synthesizing of AgNPs [6-9]. In spite of the high production efficiency, this method may be associated with environmental toxicity and biological risks of used reducing and stabilizing agents [10]. Hence, some research groups developed recently the eco-friendly approaches for the synthesis of AgNPs mainly by using of natural polymers [11-13]. On the other hand, it is necessary to synthesis of AgNPs with relatively short times. The microwave irradiation is one of the best methods in this regard. In general, the microwave-assisted synthesis of nanoparticles have well advantageous than the conventional heating methods due to uniform and rapid heating in a short time [14-17].

Recently, dye removal from wastewater has attracted much attention because discharging of dyes from various industries into water resources can cause significant color change and biomagnifications

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[18-21]. Therefore, it is necessary to remove colored contaminants from wastewater before discharging them into environment. Among a wide range of chemical and physical methods for the treatment of polluted aqueous solution [22-24], adsorption process is probably the best method because it is economically cost effective, efficient and simple [25-27]. To the best of our knowledge based on a precise survey of the Chemical Abstracts, the present paper is the first report on the using of kappa-carrageenan as reducing and stabilizing agent in the preparation of AgNPs. So, following on continuous research on modification of biopolymers [28-30], the aim of the present study is to evaluate the potential of the prepared kappa-carrageenan beads for removal of anionic dyes from aqueous solutions along with antibacterial properties.

MATERIALS AND METHODS

The polysaccharide, kappa-carrageenan (from Condinson Co., Denmark), silver nitrate (from Sigma-Aldrich Co., Germany) and crystal violet (from Difko Chemical Co., UK) were used without further purification.

Preparation of beads

Typically, one gram of kappa-carrageenan was dissolved in a 100 mL beaker containing 40 mL of distilled water. Then, an appropriate amount of $AgNO_3$ precursor solution (10 mg $AgNO_3$ in 20 mL water) was added drop wise. The reaction mixture was then placed in a microwave oven (Galanz WP750-B1, 700 W). After cooling to room temperature, the beads were finally formed by dropping the KCl solution into the mixture and allowed to stir for 1 h. A general schematically illustration of synthetic mechanism for the beads was presented in Fig. 1.

Characterization of beads

The surface morphology of the gel was examined using scanning electron microscopy (SEM). Dried superabsorbent powder were coated with a thin layer

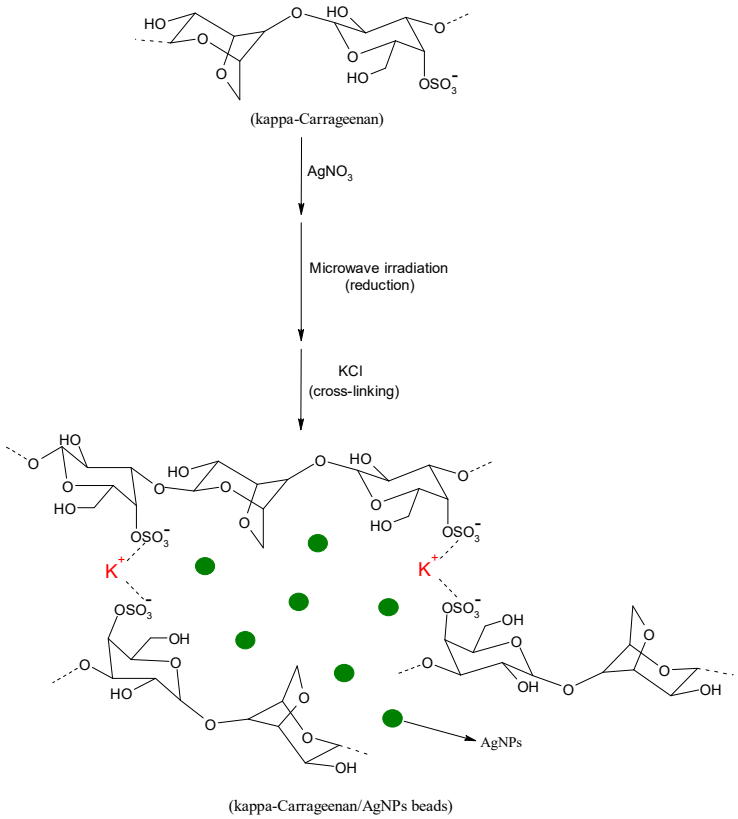

Fig. 1. Schematic illustration of microwave-assisted synthesis of beads.

of palladium gold alloy and imaged in a SEM instrument (Leo, 1455 VP). Transmission electron microscopy (TEM) micrographs were recorded with a Philips CM10 (UK) operating at 60 kV tension. The X-ray diffraction (XRD) patterns of samples were also recorded using a Siemens D-500 X-ray diffractometer with wavelength l= 1.54 A° (Cu–Ka), at a tube voltage of 35 kV and tube current of 30 mA.

Dye adsorption experiments

We used a batch equilibrium procedure for the removal of dye by beads. An accurately weighted of powdered sample (0.05±0.0001 g) was immersed into 50 mL of dye solution (50 mg L^{-1} of CV). The beads were then filtered off and the residual of concentration of the dye in the solution was determined using a Perkin Elmer Lambda 35 UV/VIS spectrophotometer at 595 nm

from the following equation:

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

where Q_e (mg g^{-1}) is the amount of dye adsorbed at equilibrium, C_0 (mg L^{-1}) is the initial dye concentration, C_e (mg L^{-1}) is the concentration of dye at equilibrium, V (L) is the initial volume of the dye solution, and m (g) is the mass of the adsorbent.

Antibacterial assay

The antibacterial activity of the synthesized beads was evaluated against two kinds of Gram bacteria using the agar disk diffusion method with determination of the inhibition zones. Briefly, the sterile paper discs (10 mm) were impregnated overnight with 40 µL of each concentration of bead samples and then left to dry at 37 °C for 12 h in sterile conditions. After this period, the impregnated discs were placed on the inoculated agar and incubated for 24 h at 37 °C. After incubation, the zone of inhibition was measured in mm by subtracting the disk diameter from the total inhibition zone diameter.

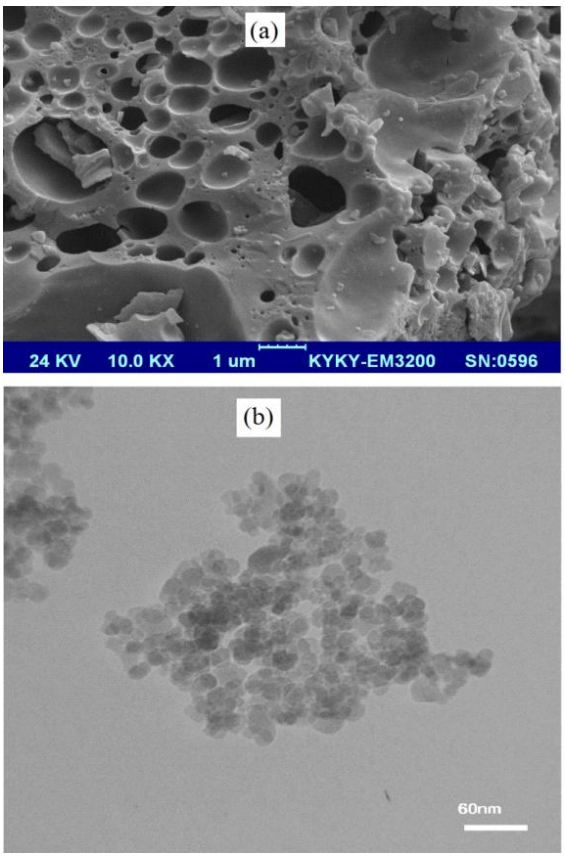

Fig. 2. The SEM (a) and TEM (b) images of the beads.

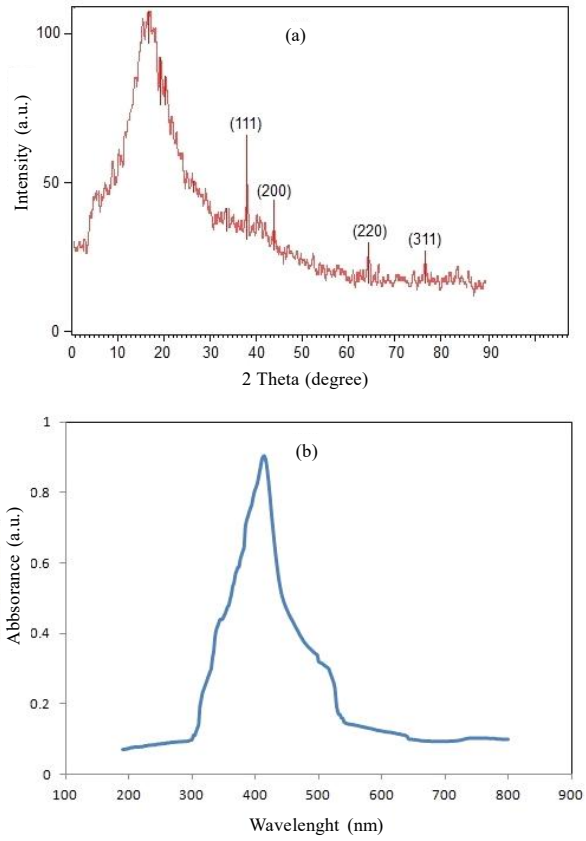

Fig. 3. The XRD pattern (a) and UV-Vis spectra (b) of the prepared beads

RESULTS AND DISCUSSION

Structural characterization of beads

Fig. 2 shows the SEM and TEM images of the obtained AgNPs loaded *kappa*-carrageenan beads. The SEM image of bead in Fig. 2a showed a porous structure characteristic of crosslinked polymeric network. The TEM micrograph (Fig. 2b) depicted that the average particle size of AgNPs was 15 nm with uniform and spherical shapes. The presence of crystalline AgNPs in the structure of the synthesized beads was also confirmed by using XRD technique. Fig. 3a displays typical XRD pattern of the beads. The distinct diffraction peaks at approximately 2q values of 38.1, 44.2, 64.3 and 77.4° are corresponded to reflections from (111), (200), (220) and (311) of the crystal planes of AgNPs, respectively. Moreover, the broad reflection at 14° is due to the crystallinity of *kappa*-carrageenan backbones. Fig. 3b shows the UV-Vis absorbance spectra of the product. The band observed at 414 nm is assigned to the unique surface plasmon resonance adsorption of the silver nanoparticles [31,32].

Dye adsorption study

In order to well-study the adsorption behavior of the synthesized beads, the dye adsorption capacities were measured as a function of solution pH, initial CV concentration, and temperature for a series of beads prepared by adjusting the feed amounts of initial materials as shown in Table 1.

Table 1. Feed compositions of the kappa-carrageenan beads.

Bead code	Feed components		
	kappa-Carrageenan (g)	$AgNO_3$ (M)	KCl (M)
S1	2.0	0.01	0.05
S2	4.0	0.02	0.15
S3	6.0	0.04	0.25

Effect of pH on dye adsorption

The pH of the initial dye solution is an important factor in adsorption process. So, we studied the effect of pH value of solution on the adsorption capacity of the beads. As shown in Fig. 4, the change in the pH of dye solution has not considerable effect onto dye adsorption uptake of beads. This behavior can be attributed to the pH-independent property of *kappa*-carrageenan component. *kappa*-Carrageenan is an anionic polysaccharide comprising sulfate groups, which are completely dissociated in the overall pH range [33]. It is necessary to mention that the pKa value of sulfate functional groups is -1.9. So, these pendants functional groups in the bead structure are completely dissociated in the overall pH range and therefore show pH-independent swelling behavior.[34] As a result, the synthesized *kappa*-carrageenan beads can be considered as novel adsorbents to eliminate various cationic dyes from wastewater in the overall pHs range.

Effect of initial dye concentration on dye adsorption

The influence of initial CV concentration on dye removal capacities of the beads was shown in Fig. 5. As observed, the Q_e values increased sharply with an increase in the initial concentration of CV dye up to 120 mg L^{-1} and then reach a plateau. This behavior can be easily attributed to the increase in the number of dye molecules in the vicinity of the beads.

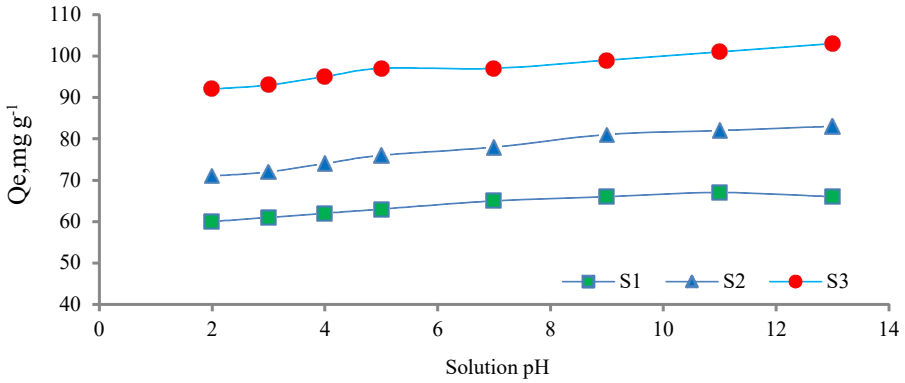

Fig. 4. Effect of pH on dye adsorption capacity of beads.

Effect of temperature on dye adsorption capacity

The effect of temperature on removal of CV dye was carried out at four different temperatures (25, 35, 45, and 55 °C). As shown in Fig. 6, the dye adsorption is considerably increased with increasing of temperature for all samples. An increase in temperature increases the rate of CV diffusion within the hydrogel nanocomposite network, indicating the adsorption process is endothermic. The thermodynamic parameters including standard Gibbs free energy

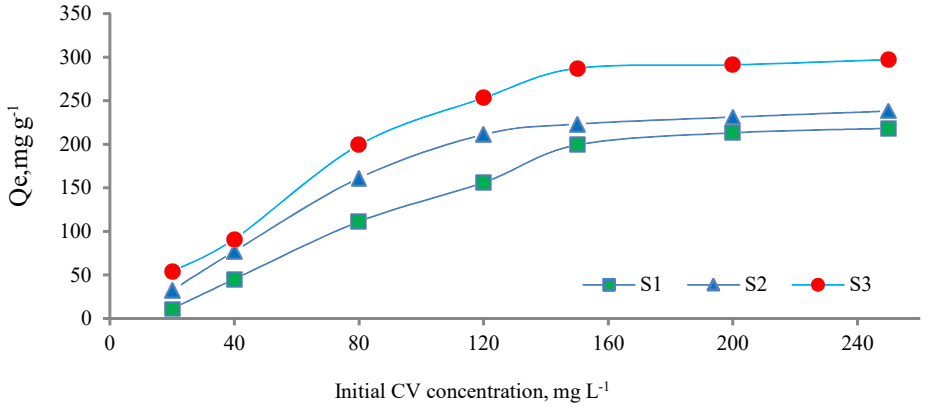

Fig. 5. Effect of initial dye concentration on CV adsorption capacity of beads.

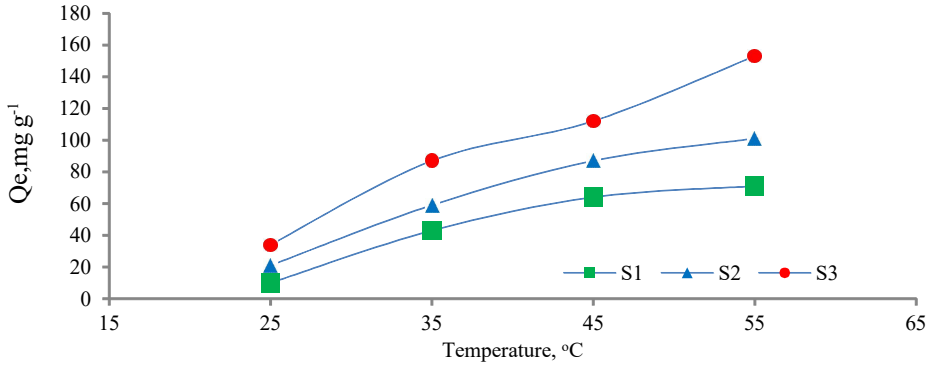

Fig. 6. Effect of temperature on CV adsorption capacity of beads.

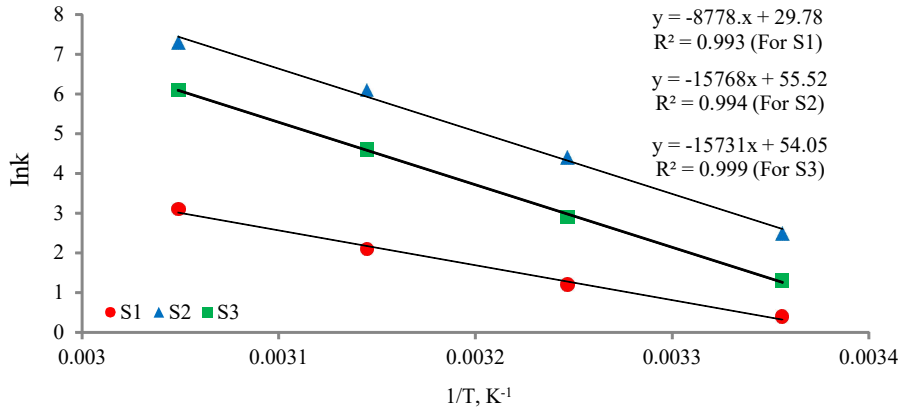

Fig. 7. Plot of LnK_L versus $1/T$.

Table 2. Thermodynamic parameters for the adsorption of CV onto bead adsorbents.

Bead code	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	ΔG^o (kJ mol^{-1})			
			298 K	308 K	318 K	328 K
S1	72.98	247.59	-0.626	-3.096	-5.566	-8.036
S2	131.09	461.59	-1.032	-4.874	-7.465	-9.387
S3	130.79	449.37	-2.746	-5.872	-8.738	-9.872

Table 3. The pseudo-first-order and pseudo-second-order adsorption kinetic parameters.

Bead code	Pseudo-first-order			Pseudo-second-order			$Q_{e\,(exp)}$
	k_1	$Q_{e\,(cal)}$	R^2	k_2	$Q_{e\,(cal)}$	R^2	
S1	0.032	87	0.8873	0.0087	214	0.9934	211
S2	0.054	97	0.8978	0.0064	242	0.9971	240
S3	0.091	117	0.8954	0.0092	271	0.9988	269

change (ΔG^o, kJ mol^{-1}), enthalpy change (ΔH^o, kJ mol^{-1}), and entropy change (ΔS^o, J K^{-1} mol^{-1}) have been also calculated from the following equations [35]:

$$Ln\ K = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (2)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (3)$$

where K is adsorption affinity, R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature in Kelvin. The values of ΔH^o and ΔS^o are obtained from the slope and the intercept of the plot of *lnK* versus *1/T*, respectively (Fig. 7 and Table 2). The ΔG^o values are then calculated from Eq. (3). Results of the calculations are also shown in Table 2. For all samples, the values of ΔG^o at all temperatures are negative during the adsorption process. This confirms that the adsorption is thermodynamically favorable and spontaneous. The positive values of ΔH^o and ΔS^o also demonstrate that the adsorption is endothermic with probability of a favorable adsorption [36].

Dye adsorption kinetics

One of the most important parameters to evaluate the adsorption efficiency of adsorbent materials is kinetic of dye removal. To study the adsorption kinetics, pseudo-first-order and pseudo-second-order kinetic models were used. The pseudo-first-order rate equation is given as [37]:

$$Ln\ (Q_e - Q_t) = Ln\ Q_e - k_1 t \quad (4)$$

The pseudo-second-order rate equation is given also as [38]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (5)$$

where Q_t and Q_e (mg g^{-1}) are the theoretical amounts of adsorbed dye by the beads at time *t* and equilibrium, respectively. k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the adsorption rate constants for the pseudo-first-order and the pseudo-second-order models, respectively.

The kinetic data were fitted with both models and the results are summarized in Table 3. The values in Table 3 were calculated from a plot of $Ln(Q_e-Q_t)$ *versus* *t* for the pseudo-first-order and from a plot of t/Q_t versus *t* for the pseudo-second-order model (not shown). According to Table 3, a linear relationship with high correlation coefficients ($R^2 \geq 0.9934$) was obtained, which suggests that the kinetic data of CV adsorption on beads can be described by the pseudo-second-order kinetic model. Moreover, the values of the calculated adsorption capacities ($Q_{e,cal}$) by the pseudo-second-order kinetic were closer to those determined by experiments ($Q_{e,exp}$).

Dye adsorption isotherms

In general, the adsorption isotherms demonstrate the interaction between solute and the adsorbent and give an idea of the adsorption capacity. So, we used two well-known sorption isotherm models, i.e. Langmuir and Freundlich, to fit the experimental data according to the following Eqs [39]:

$$\frac{C_e}{Q_e} = \frac{1}{(K_L Q_m)} + \frac{C_e}{Q_m} \quad (6)$$

$$LnQ_e = LnK_F + \frac{1}{n} LnC_e \quad (7)$$

where C_e (mg L^{-1}), Q_m (mg g^{-1}), K_L (L mg^{-1}), K_F [(mg g^{-1}) / (mg L^{-1})$^{1/n}$] and *n* are the equilibrium dye concentration,

Table 4. Langmuir and Freundlich isotherm parameters for adsorption of CV by the beads.

Bead code	Langmuir isotherm model			Freundlich isotherm model		
	Q_m	K_L	R^2	n	K_F	R^2
S1	231	1.257	0.9968	0.523	24.65	0.8834
S2	239	1.687	0.9958	0.547	54.28	0.8954
S3	243	1.054	0.9981	0.943	32.87	0.8887

Table 5. Average of inhibition zone (mm) of the beads containing different content of *kappa*-carrageenan and AgNPs against two bacterial pathogens.

Bead sample	Inhibition zone (mm)	
	E. coli	*S. aureus*
A (containing 1.5% kappa-carrageenan and 10% AgNPs)	11.2	13.4
B (containing 0.5% kappa-carrageenan and 5% AgNPs)	7.4	9.1

the maximum monolayer adsorption capacity, the Langmuir constant, the Freundlich constant and an empirical constant, respectively.

The calculated adsorption isotherm constants from the plot of C_e/Q_{e-} *versus* C_e and a plot of Ln Q_e *versus* Ln C_e were listed in Table 4. The data depict that the Langmuir model displayed the best fit with the higher R^2 values when compared to the Freundlich isotherm. Therefore, the dye removal by the synthesized beads takes place through monolayer adsorption due to the homogenous distribution of active sites on the adsorbent surface.

Antibacterial activity

The antibacterial activity of beads was tested using two Gram bacteria (*E. coli* and *S. aureus*) using the disk diffusion technique. The results are summarized in Table 5. It is observed that the synthesized beads in this work loaded with AgNPs have high antibacterial activity. This behavior can be attributed to the presence of silver nanoparticles with high surface area which enabled beads to reach easily and rapidly the nuclear contend and the cell wall of bacteria [40]. Meanwhile, it is apparent from the data in Table 3 that the bead prepared with 1.5% *kappa*-carrageenan and 10% AgNPs (sample A) has higher antibacterial activity than those synthesized with 0.5% *kappa*-carrageenan and 5% AgNPs (sample B).

CONCLUSION

In the present study, the microwave technique as a facile and efficient method was adopted for the synthesis of highly AgNPs via in situ reduction of silver nitrate in the presence of kappa-carrageenan as reducing and stabilizing agent. The cross-linking reaction was done simply with K^+ cations. The surface morphology and nanostructural properties of the beads were confirmed using SEM, TEM, XRD, and UV-Vis techniques. Conclusively, the applied method is simple and cost-effective and does not use any hazardous and toxic chemicals unlike other methods. From the practical viewpoint, the prepared beads are economic and high potential adsorbents for removal of various cationic dyes from aqueous solutions in overall pH range as well as suitable materials for antibacterial applications.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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