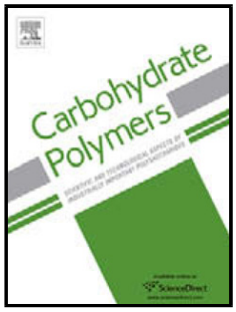

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Clean approach to synthesis of graphene like $CuFe_2O_4$@polysaccharide resin nanohybrid: Bifunctional compound for dye adsorption and bacterial capturing

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Highlights

- Solid state combustion rout was used for copper ferrite synthesis.
- Graphene like polysaccharide resin was synthesized using glucose and citric acid.
- Solid state solvent free rout was used to prepare magnetic resin.
- Dye adsorption and antimicrobial activity of magnetic resin was studied.

Abstract

Focus of this research is on employment of a green route to prepare magnetic $CuFe_2O_4$@polysaccharide resin for environmental remediation purpose. The method is including solvent free solid state synthesis of copper ferrite nanoparticles by combustion route using cellulose as fuel. Then polysaccharide resin as well as its magnetic composite was prepared by using glucose, citric acid and copper ferrite as solid raw materials. Characterization study using FESEM and TEM images showed that as synthesized resin possesses graphene like structure as ferrite nanoparticles are dispersed in the matrice of resin. Methylene blue (MB) adsorption study of the nanohybrid showed that maximum removal efficiency obtained at pH = 8 with very fast

equilibrium time of 1 min. Kinetic study confirmed pseudo – second order model is dominant kinetic model for dye removal. Moreover isotherm study revealed dye adsorption followed Freundlich model with maximum adsorption capacity of 366.6 mg g^{-1}. Antibacterial activity of resin and magnetic composite was examined and result confirmed high efficiency of them in coping with E. coli as sample pathogen. Effect of solution pH, contact time and adsorbent dosage on E.coli capturing efficiency was also studied. Results showed bacteria capturing is more than 99% within equilibrium time of 20 min and dosage of 20 mg which confirmed high efficiency of the nanosystem in bacteria removing.

Keywords: copper ferrite, polysaccharide, solvent free, green chemistry, methylene blue, antimicrobial.

1. Introduction

Clean chemistry term, also known as environmentally benign or green chemistry, was submitted to United States scientific communities in 1991(W Wardencki, Curylo, & Namiesnik, 2005). This approach emphasizes on manners that reduces threats to environment and life health. In other words applied synthetic routes in clean chemistry should employ as well as produce materials with little or no toxicity to ecosystem(Tang, Smith, & Poliakoff, 2005) hence in recent decades solvent – less techniques, catalyst usage as well as synthesis of biodegradable materials have been widely employed in material synthesis (Polshettiwar & Varma, 2010; Waldemar Wardencki & Namies, 2000; W. D. Zhang, Xiao, Zhu, & Fu, 2009). Based on the above concepts there are several reports in literature for sustainable synthesis and modification of nanomaterials. For example Jin et al (Yinying Jin et al., 2013) and Wu et al (Q. Wu et al., 2014) used solvent less method for zeolite synthesis. Dyke and Tour employed a solvent free method for carbon nanotube functionalization(Dyke & Tour, 2003) moreover, Siemion et al (Siemion, Kapuśniak, & Kozioł, 2005) used solid state route to prepare cationic starches. Despite worthiness of these reports, the energy efficiency was not considered by them. In other words, the reported works show potential environmental risks (Lu, Shen, Xie, & Zhang, 2010).

In recent decades increasing interests were devoted to biosorption process which employs biological materials in environmental remediation. In fact this process as a low price and non hazardous technique with ease of construction and maintenance characteristic uses biodegradable materials with natural abundant (Asadi, Shariatmadari, & Mirghaffari, 2008; BULUT & TEZ, 2007; Chathuranga, Dissanayake, Priyantha, Iqbal, & Iqbal, 2014; L. Jin & Bai, 2002; Taylor, Chen, Ding, & Nie, 2012) as a result, it can be considered as a clean method. However, pretreatment and modification of biosorbents before use is the main restrict of biosorption system since at treatment process concentrated acid - base or other chemical reactant usage are inevitable (Akar, Yilmazer, Celik, Balk, & Akar, 2015; Jakóbik-Kolon, Milewski, Mitko, & Lis, 2014; Koyuncu & Koyuncu, 2017; Sahraei, Pour, & Ghaemy, 2017; Sayğılı & Güzel, 2016). This weakness can be rectified by sustainable synthesis of biomaterials from initial natural reactants. Based on the mentioned principal of clean chemistry, in this work a sustainable solid state route was employed to prepare polysaccharide resin. This is the first report for polysaccharide resin generation by solid state route using citric acid and glucose as initial reactants. The resin was candidate for water treatment hence to made adsorption process easier and simpler, magnetic composite of resin was also prepared. Starting reagents for resin preparation are abundant in nature, moreover prepared polysaccharide possess biodegradability and low toxicity(Lotfy, Ghanem, & El-helow, 2007; Shendurse & Khedkar, 2016) which made it more effective for environmental remediation. The magnetic component of nanocomposite is inverse spinel ferrite, $CuFe_2O_4$, which was synthesized by solid state combustion rout using cellulose as fuel. In fact a low toxic reagent with a simple facial solid state technique was employed for $CuFe_2O_4$ synthesis which made the process more economic. In the ferrite structure octahedral sites were occupied with 8 Cu^{2+} ions while 16 Fe^{3+} ions are equally distributed between tetrahedral and octahedral sites (Agouriane et al., 2016; Jiang, Goya, & Rechenberg, 1999). Selection of copper ferrite was based on the fact that it possesses super paramagnetic and antibacterial characteristic, as well as high thermal stability (Iqbal, Yaqub, Sepiol, & Ismail, 2011).

Dye adsorption property and antimicrobial activity of $CuFe_2O_4$@polysaccharide resin as multifunctionality material was studied. This is the first report for application of synthetic $CuFe_2O_4$@polysaccharide resin in water treatment especially as bifunctional nanocomposite for

dye and bacterial capturing. Methylene blue (MB) was used as a model dye since it is most applied ones for industrial applications whereas their products are not easily biodegradable and expose to them causes series physiological response (Hassan, Abdel-mohsen, & Fouda, 2014; Jian, Qingwei, Meihong, Haiqiang, & Na, 2013; Li et al., 2013; Maatar & Boufi, 2017; Parrott, Bartlett, & Balakrishnan, 2016; Postai et al., 2016; Wang, Cai, & Zhang, 2014; X. Wu, Shi, Zhong, Lin, & Chen, 2016). Antibacterial activity of resin and composite was examined with capturing of *Escherichia coli* (E.coli). The E.coli is a gram-negative bacterium that is widely distributed in nature (From, Pukall, Schumann, & Granum, 2005; Sadeghi-Kiakhani & Safapour, 2015) hence elimination of it is vital in environmental safety and human health. Effective parameters on dye and bacteria capturing including pH, time and adsorbent dosage was studied and optimum levels of them were reported and discussed in details.

2. Experimental

2.1. Materials and instruments

Citric acid, Glucose, cellulose, MB, $Fe(NO_3)_3.9H_2O$ and $Cu(NO_3)_2.3H_2O$ was supplied from Merck, (Darmstadt, Germany). MB solution (1000 mg L^{-1}) was prepared by dissolving it in desired amount of distilled water. HCl and NH_3 solution (0.1 mol L^{-1}) was used for pH adjustment.

The prepared ferrite nanoparticles, resin and $CuFe_2O_4$@polysaccharide resin were characterized by powder X-ray diffraction analysis (XRD), Field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM), Fourier transforms infrared spectra (FT-IR), elemental mapping, Raman spectroscopy, BET surface area and vibrating sample magnetometry (VSM). XRD was recorded with Phillips powder diffractometer, X' Pert MPD, using Cu-Kα radiation at λ=1.540589 Å. FESEM, elemental mapping and TEM carried out using SIGMA VP ZEISS and Zeiss - EM10C instruments. FT - IR was measured with Equinox 55 Bruker at the wavenumber of 400-4000 cm^{-1}. VSM was recorded with Lake Shore Model 7400, Japan. Raman spectra were recorded with Nd: YAG laser, Takram P50C0R10 – Teksan. The N_2 adsorption–desorption isotherms were recorded on a Nova Station A system. A digital pH-meter (model 692, metrohm, Herisau, Switzerland), was used for the pH adjustment.

A Lambda – 25 UV – Vis spectrophotometer was used for recording the dye adsorption characteristic.

2.2. Synthesis of ferrite nanoparticles, polysaccharide and nanocomposite

A simple solid state combustion route was employed for synthesis of $CuFe_2O_4$ nanoparticles. For this purpose 0.60 g of $Cu(NO_3)_2.3H_2O$ and 2.0 g $Fe(NO_3)_3.9H_2O$ have been mixed in a mortar for 2 min until a uniform pasty mixture was obtained then 1.0 g of cellulose was added to metal salt and mixed for 15 min followed with combustion at 150ºC for 5 min. To remove the residual of carbon and nitrate from ferrite structure the nanoparticles were heated under constant air at 500 ºC for 1h. To prepare polysaccharide resin 0.5 g of glucose and 0.5 g of citric acid was mixed in a mortar for 10 min then was heated under constant air at 155°C for 2h followed with annealing at 200°C for 5h. To prepare $CuFe_2O_4$@polysaccharide resin, 0.5 g of $CuFe_2O_4$ was added into 1.0 g of glucose - citric acid mixture (1:1) and completely mixed for 10 min. The materials were placed in a furnace and heated at 155°C for 2h followed with annealing at 200°C for 5h. After cooling to room temperature, as synthesized nanohybrid was stored for subsequent usage.

2.3. Dye adsorption experiment

Batch method was used to perform MB adsorption experiments. In typical runs 10 mL of MB solution with initial concentration of 10 – 400 mg L^{-1} were used. After pH adjustment at 8.0, 30 mg of $CuFe_2O_4$@polysaccharide resin was added and shacked for 1.0 min. After collection of the sorbent, MB concentration in supernatant was determined with measuring absorbance at λ_{max} = 664 nm by UV- Vis spectrometer and removal percentage (%R) was calculated by the following equation.

$$\%R = (C_0 - C_e) \times 100/C_0 \quad (1)$$

At this equation C_0 (mg L^{-1}) and C_e (mg L^{-1}) represent initial and remained dye concentration in the solution, respectively.

2.4. Antibacterial activity

To evaluate antibacterial activity of as synthesized resin and $CuFe_2O_4$@polysaccharide resin, Gram-negative strain, E.coli (supplied from Institute Pastor, Tehran, Iran) was used as a model pathogen. 100 mL of Luria Broth (LB; consisting of 5 g L^{-1} bacto-yeast extract, 15 g L^{-1} tryptone and 5 g L^{-1} NaCl) was used as growth medium to cultivate E.coli. After shack the strains in an incubator at 30°C for 32 h, cells were then separated by centrifugation (4000g for 10 min at 4°C). After washing the bacterial pellets with 0.9% of NaCl at pH 7.0 they were re-suspended in the physiological saline to obtain cell density of 1.5×10^8 Colony Forming Unit per milliliter (CFU mL^{-1}). Sterilized physiological saline was applied as bacterial capture medium with the aid of batch method. For this purpose 20 mg of resin or $CuFe_2O_4$@polysaccharide resin was added in the 20 mL bacteria solutions with concentration of 1.5×10^8 CFU mL^{-1}. The mixture was incubated for 20 min then the particles were separated from the suspension. In the following 1.0 mL of supernatant was collected and analyzed for bacterial concentration via colony counting method. Bacteria capture efficiency was determined by counting of colonies before and after capturing experiment.

3. Results and discussion

3.1. Characterization

The TEM image of resin at Fig.1a and 1b proves that resin possesses lamellar graphene like slim sheets. Moreover, according to the TEM image of the $CuFe_2O_4$@polysaccharide resin at Fig.1c and 1d magnetic nanoparticles are dispersed as dark spots in composite structure. Formation of layer structure is owed to crosslinking between citric acid and hydroxyl functional groups of glucose through esterification reaction. In other words structure of citric acid and glucose contains several carboxylic acid and hydroxyl groups which condense with each other at various directions. Tang et al deduced that carbohydrates with C, H and O in the ratio of 1: 2: 1 can be used as carbon sources to prepare graphene like structures (Libin Tang, Xueming Li, Rongbin Ji, Kar Seng Teng, Guoan Tai, Jing Ye, 2012). In fact hydrogen and oxygen in the forms of hydroxyl, carboxyl or carbonyl generate graphene like structure under dehydrate reaction. Heating of glucose and citric acid causes removal of water and polymerization into high molecular weight compounds. Moreover, citric acid induces hydroxymethylfurfural formation

from glucose which consists of a furan ring (Yuriy Roma´n-Leshkov, Juben N. Chheda, 2006) which can also participate in polymerization process. Generation of stacked layers is as a result of van der Waals force between individual layers (Alijani & Shariatinia, 2017) owe to the interaction between methylene groups as well as hydrogen bonding of oxygen-containing functional groups (C–O, C=O, and−OH) at the structure of polysaccharide resin.

The interaction between glucose and citric acid for synthesis of resin was further studied with FT – IR study. The spectrum of glucose, citric acid and resin at the wavenumber of 600 – 3500 cm^{-1} is shown at Fig.2. The spectrum of glucose show vibration of aggregated –OH due to hydrogen bonding, vibration of CH and stretching of C–OH groups at 3264, 2944 and 1000 -1500 cm^{-1}, respectively. At the spectrum of citric acid vibration of C=O as the main characteristic of carboxylic acid appeared at 1712 cm^{-1}. The spectrum of resin showed some changes relative to glucose and citric acid. At first look can be seen that the vibration of OH at 3000 – 3500 cm^{-1} divided to two distinct peaks corresponding to aggregated OH at 3272 cm^{-1} and free OH group at 3490 cm^{-1}. This change can be owed to the breaking of hydrogen bonding between hydroxyl groups as a result of new structure generation. Other main change is transfer of C=O stretching from 1712 cm^{-1} to 1743 cm^{-1} owing to change in carbonyl vibration source from carboxylic acid to ester structure. The intensity of C=C at 1690 cm^{-1} also increased which can be assigned to aromatic backbone of furfural ring. Increase in the peak intensity at 650 – 900 cm^{-1} can also be assigned to CH deformation in aromatic ring. Moreover, the sharp peak at 1136 cm^{-1} can be assigned to C – O vibration in ester structure. All mentioned evidence proves condensation reaction between hydroxyl/carboxyl groups of glucose and citric acid.

The N_2 adsorption–desorption isotherm for resin and $CuFe_2O_4$@polysaccharide resin as well as corresponding Barrett, Joyner and Halenda (BJH) pore-size distribution curve is shown at Fig. 3. As can be seen the curve for resin show type II isotherm with a minor hysteresis loop as a result of filling and emptying of the mesopores by capillary condensation(Bayat, Beyki, & Shemirani, 2015). This type of isotherm illustrates slit shape pores with parallel walls. The curve for $CuFe_2O_4$@polysaccharide resin show type IV isotherm that illustrates tapered slit pore.

Table 1 shows the BET characteristics of the materials. As can be seen, the pore diameter of the material are in the range of 3 – 6 nm and pore size decreased from resin to composite. According to the pore-size distribution the materials are classified as mesopores compounds (Dabrowski, 2001). Moreover it can be seen that the total pore volume of composite was less than resin because of pore occupation by the ferrite nanoparticles.

3.2. Dye adsorption

3.2.1 Effect of pH on dye adsorption

In adsorption process solution pH is a main factor which affects the efficiency of sorbent for adsorption of target analyte. In other words pH can impress both adsorbate and adsorbent functional groups resulting to increase or decrease adsorption efficiency hence effect of pH on dye adsorption was studied in the range between 2 to 9. To evaluate the effect of this parameter, 10 mL of MB solution with initial concentration of 10 mg L^{-1} was employed. Amount of sorbent and shacking time were fixed in 30 mg and 10 min, respectively. After equilibrium the sorbent was collected with external magnetic field and concentration of MB in supernatant was determined and removal percentage was calculated. Results for effect of pH on MB adsorption are shown at Fig. 4a.

The results revealed that adsorption efficiencies are approximately constant in the studied pH range as removal percentage is 92.8% at pH of 2 which reaches to 95% at pH of 8. Some increase in removal efficiency with increase of pH is owe to the fact that rising solution pH causes deprotonation of polar functional groups on sorbent surface which generate negative charge on the sorbent surface. This situation is in favorite of cationic dye adsorption by electrostatic interaction. High adsorption efficiency at acidic solution confirmed that adsorption mechanism is beyond of sole electrostatic attraction. Ion exchange also can be considered as a mechanism since at acidic solution protons (H^+) on the sorbent surface can be replaced by MB from solution. Hydrophobic interaction between methylene groups of sorbent and dye is another mechanism [54]. Other main mechanism i.e., π-π interactions between C=O and C=C groups of sorbent and MB also strongly attract MB onto sorbent surface. Hydrogen bonding is another reason for effective adsorption of MB. In other words, the sorbent has potential H-bonding sites i.e., C=O, -OH groups which share H – bonding with nitrogen groups in MB structure. In brief,

π-π and hydrogen bonding as well as ion exchange and hydrophobic interaction along with electrostatic attraction are potential adsorption mechanism for dye uptake by the nanocomposite.

3.2.2 Adsorbent dosage

It is necessary to optimize adsorbent dose to maximize the interactions between dye and active sites of the adsorbent. The effect of adsorbent dosage on the removal efficiency is shown in Fig. 4b. It can be seen that the removal efficiencies enhanced as the dosages of sorbent increased from 5 to 30 mg, and then no further increase in adsorption efficiency is observed by increasing adsorbent dosage up to 35 mg. Consequently, 30 mg of the nanocomposite is selected as the optimum adsorbent amounts for the dye removal.

3.2.3. Effect of time on dye adsorption

Adsorption of MB by the $CuFe_2O_4$@polysaccharide resin was performed between 1 to 10 min shacking times at initial concentration of 10 mg L^{-1} and adsorbent dosage of 30 mg. According to the result at Fig. 4c MB removal is approximately independent from shacking time since removal percentage is 95% at first one minute which didn't significantly changed with increasing time up to 10 min. Fast adsorption equilibrium is owe to accessibility of the adsorption sites as well as presence of external surface adsorption in absence of diffusion resistance.

3.3. Bacterial capturing

3.3.1. Effect of pH on bacteria capturing

Bacterial cell capture efficiency can be affected greatly with the pH of solution hence the influence of pH on E.coli adsorption efficiency was studied. Initial bacterial concentration was 1.5×10^8 CFU mL^{-1} and solution pH was at three levels including 3, 5 and 8. Resin and $CuFe_2O_4$@polysaccharide resin dosage was 30 mg and shacking time was 30 min. The removal percentages (%R) were obtained by culturing 1.0 mL of diluted stock sample solution or supernatant (10^{-6} time) in LB agar plates using following equation:

$$\%R = 100 \times (CFU_0 - CFU_t)/CFU_0 \qquad (2)$$

where CFU_0 is initial colony numbers and CFU_t is the number of unabsorbed colonies in the supernatant (El-boubbou, Gruden, & Huang, 2007; Zhan et al., 2014). Results in Fig. 5a,

showed that capturing efficiency is more than 99% at the studied pH range and is independent from pH. High capturing efficiency at all studied pH is owing to the presence of multiple mechanisms for bacteria capturing by the resin and $CuFe_2O_4$@polysaccharide resin. In other words the structure of resin is composed from various functional groups including methylene, carboxylic acid, carbonyl and hydroxyl groups. These functional groups are ready to capture bacteria through hydrophobic interaction, electrostatic attraction and hydrogen bonding. Hydrophobic interaction is the first one which attracts bacterium onto sorbent surface as a result of interaction between methylene groups in composite structure and lectin of bacteria. Hydrogen bonding formation between the methyl side chains/carboxyl oxygen of the bacteria cell membrane and the hydroxyl groups present on the surface of nanocomposite also contribute to capture of bacteria (Yinjia Jin, Liu, Shan, Tong, & Hou, 2014). Moreover, ferrite nanoparticles at the structure of nanocomposite have potential of killing of bacteria. Electrostatic attraction is another mechanism in acidic solutions. In other words the cell walls of E.coli have negative charge with isoelectric point of pH 3.1 (Horká, Růžička, Holá, & Šlais, 2006) which means the functional groups on the cell surface is in deprotonated form at the studied pH range which can be adsorbed on the protonated surface of sorbent with electrostatic interaction. It can be estimated that capturing efficiency should be decreases with increasing pH since at alkali solution the adhesion forces between bacteria and solid surface decreases (Denis, Touhami, & Dufre, 2002). But according to results the capturing efficiency is also more than 99% at pH of 8. This can be explained with the fact that at the alkaline solutions the highly ionized carboxylate groups on the bacteria cell surface electrostaticaly binds with positive Fe and Cu ions on the ferrite structure which induce the large adhesion force (Javad Malakootikhah, Ali Hossein Rezayana, Babak Negahdari, Simin Nasseri, 2017; Sheng, Ting, & Pehkonen, 2008). Sheet like structure also assist more efficient antibacterial characteristic. After bacteria deposition on the surface of resin nanosheets, the sharp edge of nanosheets serve as “cutters” to disrupt bacterial cell membranes, causing release of intracellular contents and cell death(Liu et al., 2011).

3.3.2. Effect of time on bacteria capturing

The effect of time on E.coli capturing efficiency was studied at initial concentration of 1.5×10^8 CFU mL^{-1} with dosage of 30 mg at pH=7 in 20 mL physiological saline and the results were given in Fig.5b. Results showed that capture of the bacteria occur effectively within first 10 min with capture efficiencies more than 70% which reached to 99% after 20 min. For further works

the time of 20 min was selected as equilibrium time. It is known that interaction energy barrier and diffusivity can affect kinetic of adsorption (Gao, Lin, & Yao, 2006). In other words penetrate of nanomaterial on cell membrane of bacteria exert main role on bacteria capturing (Pan et al., 2007). At this work the surface of resin and nanohybrid is covered with hydroxy functional groups which can easily penetrate on the bacteria cell surface moreover sheet like structure of nanohybrid can facilitate bacteria adhesion on the sorbent surface. Besides interaction of bacteria lectin with Fe and Cu cations on the composite structure induce the large adhesion force which overcome energy barriers for bacteria adsorption onto the sorbent surface (W. Zhang, Rittmann, & Chen, 2011).

3.3.3. Effect of dosage on bacteria capturing

The effects of nanohybrid and resin dosage on E.coli capturing at initial concentration of 1.5 $\times 10^8$ CFU mL^{-1} were examined at adsorbent dosage of 10 –30 mg. Equilibrium time and pH was 20 min and 7, respectively. Results are depicted at Fig.5c. It can be seen that the capture efficiency increased from 80% at dosage of 10 mg to more than 99% at dosage of 20 mg. Increases in capturing efficiency with increase in dosage could be attributed to the increase in value of accessible functional groups at higher adsorbent dosage. At the optimum conditions of pH = 7, time of 20 min and dosage of 20 mg and initial bacteria concentration of 1.5 $\times 10^8$ CFU mL^{-1} capturing experiment was performed and results at Fig. 6 showed that at obtained optimum conditions capturing efficiency is complete (100%) which confirmed the efficiency of nanocomposite for bacteria removal from aqueous solutions.

3.4. Dye and bacteria adsorption from natural water samples

To evaluate the effect of complex matrices on bacteria capturing and dye adsorption capability of nanocomposite adsorption of MB and E.coli from river and sea water (Caspian Sea) sample was studied. For dye adsorption experiment 10 mL of MB solution with initial concentration of 20 and 50 mg L^{-1} was prepared using river and sea water instead of distilled water. pH was adjusted to 8 and 30 mg of nanohybrid was added and after shacking for 1 min the sorbent was collected and dye concentration on supernatant was determined. For bacteria capturing experiment sea and river water samples was sterilized and 20 mL of them was employed. 20 mg of nanohybrid was added in the E.coli solution with concentration of 1.5 $\times 10^8$ CFU mL^{-1} at pH of 7 and after incubation for 20 min 1.0 mL of supernatant was analyzed via filter membrane

method. Results showed that MB removal efficiency was 95% at river water and 93% at sea water samples at both examined initial concentration. Bacteria capturing efficiency was more than 99% in river and sea water samples. These results confirmed the efficiency of nanohybrid for water treatment purpose.

4. Conclusions

Briefly, in this research a clean approach was employed to synthesis of $CuFe_2O_4$, polysaccharide resin and its magnetic composite. Sustainable solid state route was used to prepare graphene like resin using glucose and citric acid as green, biocompatible and nature abundant reactants. The applied method, employed reactants and generated compounds possess low toxicity to human beings and the environment. Moreover, prepared composite material was used for very fast adsorption of methylene blue dye with low equilibrium time of one minute and adsorption capacity of 366.6 mg g^{-1}. Moreover dye adsorption followed Freundlich isotherm model with multilayer mechanism. Antibacterial activity of resin and nanocomposite was examined using E.coli as sample pathogen. Effective parameters on bacteria capturing was also optimized. Results showed approximately complete (> 99%) bacterial capturing efficiency by both materials. Based on the results it can be concluded that as prepared nanocomposite has potential to be employed as multifunctional material for water treatment.

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Figure captions

Fig.1 TEM image of resin (a, b) and magnetic composite (c, d).

Fig.2 FTIR spectra of glucose, citric acid and resin.

Fig.3 The N_2 adsorption – desorption isotherm and BJH curve of resin (a) and $CuFe_2O_4$@polysaccharide resin (b).

Fig.4 Effect of pH on MB adsorption (a) conditions: adsorbent 30 mg; time 10 min; volume 10 mL. Effect of time on MB adsorption (b) conditions: adsorbent 30 mg; volume 10 mL; pH = 8 and effect of adsorbent dosage on MB adsorption (c) conditions: time 1 min; volume 10 mL; pH= 8.

Fig.5 Effect of pH on bacterial capturing efficiency (a) conditions: adsorbent 30 mg; time 30 min; volume 20 mL. Effect of time on bacterial capturing efficiency (b) conditions: pH = 7, dosage 30 mg, and effect of adsorbent dosage on bacterial capturing efficiency (c) conditions: pH = 7, time 20 min.

Fig.6 Photographs showing the bacterial culture plates of control and after treatment with nanocomposite. Plates a, c are 10^{-6} and 10^{-7} time diluted control solution of bacteria with initial concentration of 1.5×10^8 CFU mL^{-1} and plates b, d are 10^{-6} and 10^{-7} time diluted solution after treatment with 20 mg of sorbent at pH of 7 and time of 20 min.

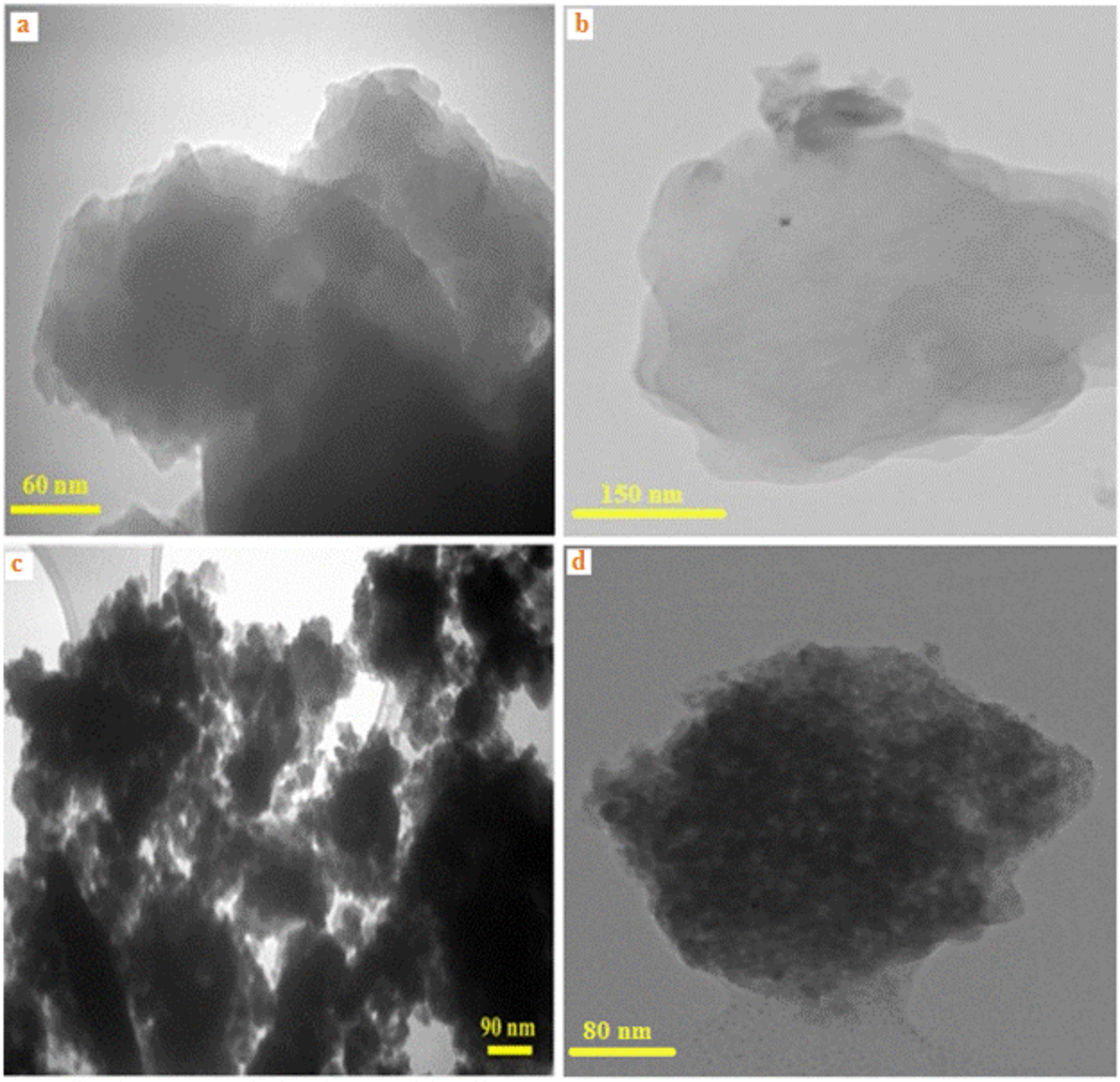


Fig.1

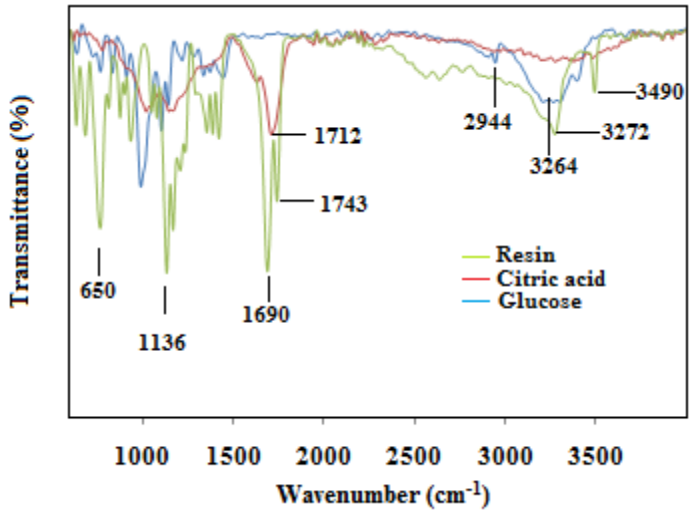
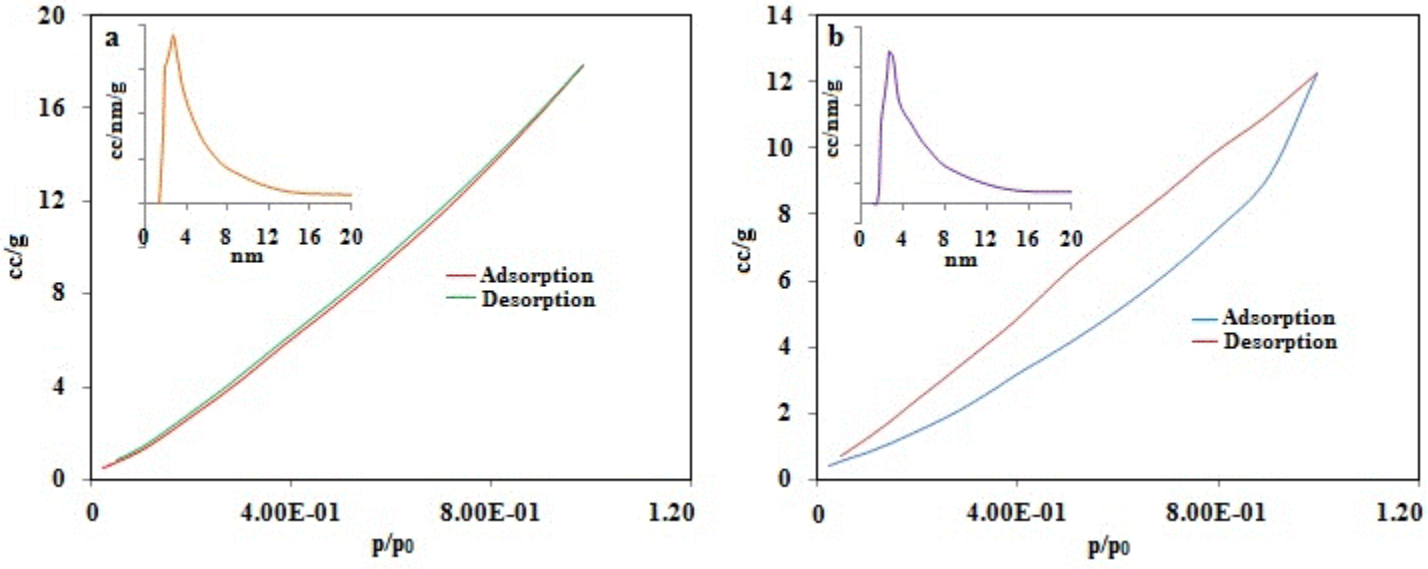


Fig.2



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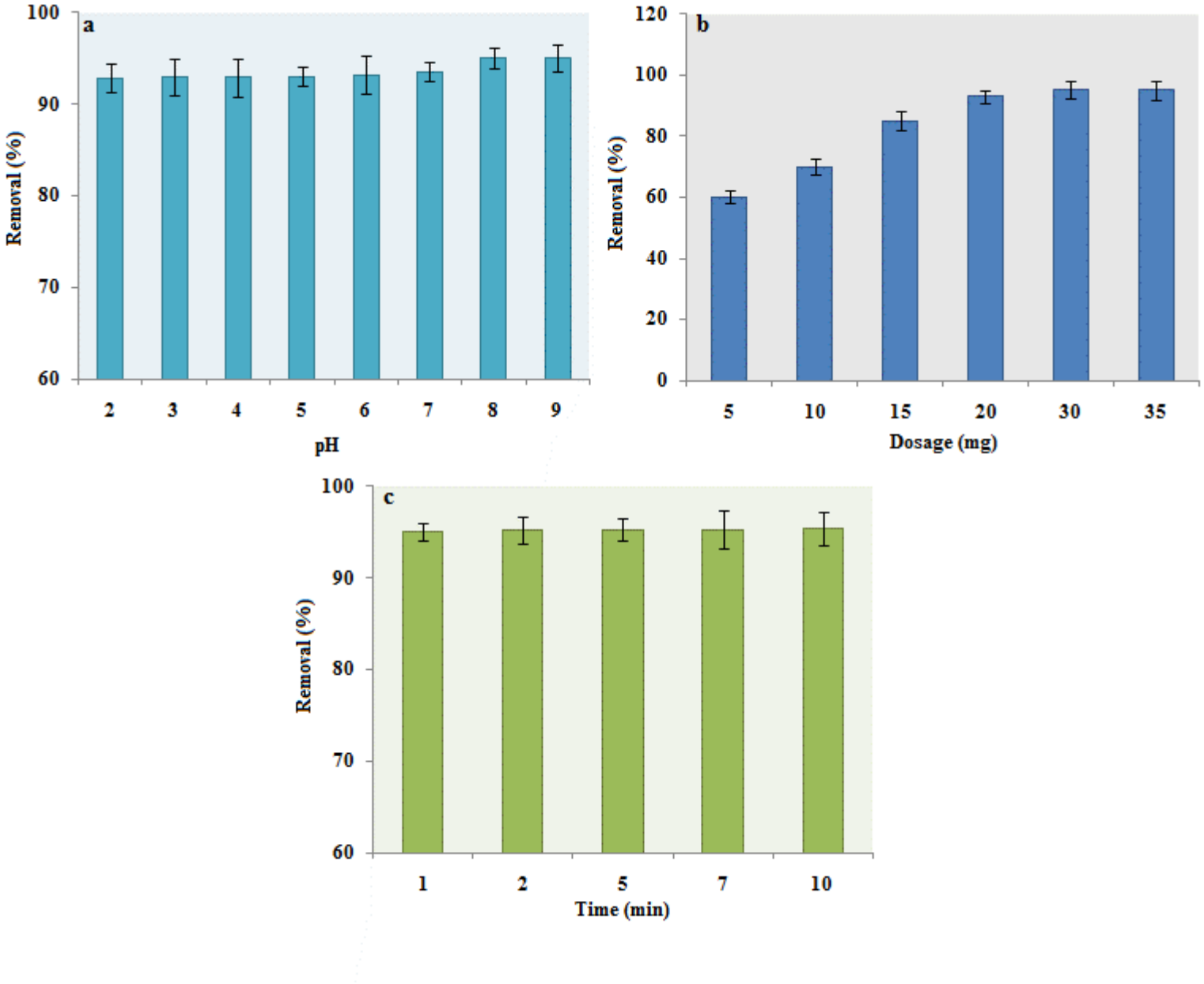

Fig.4

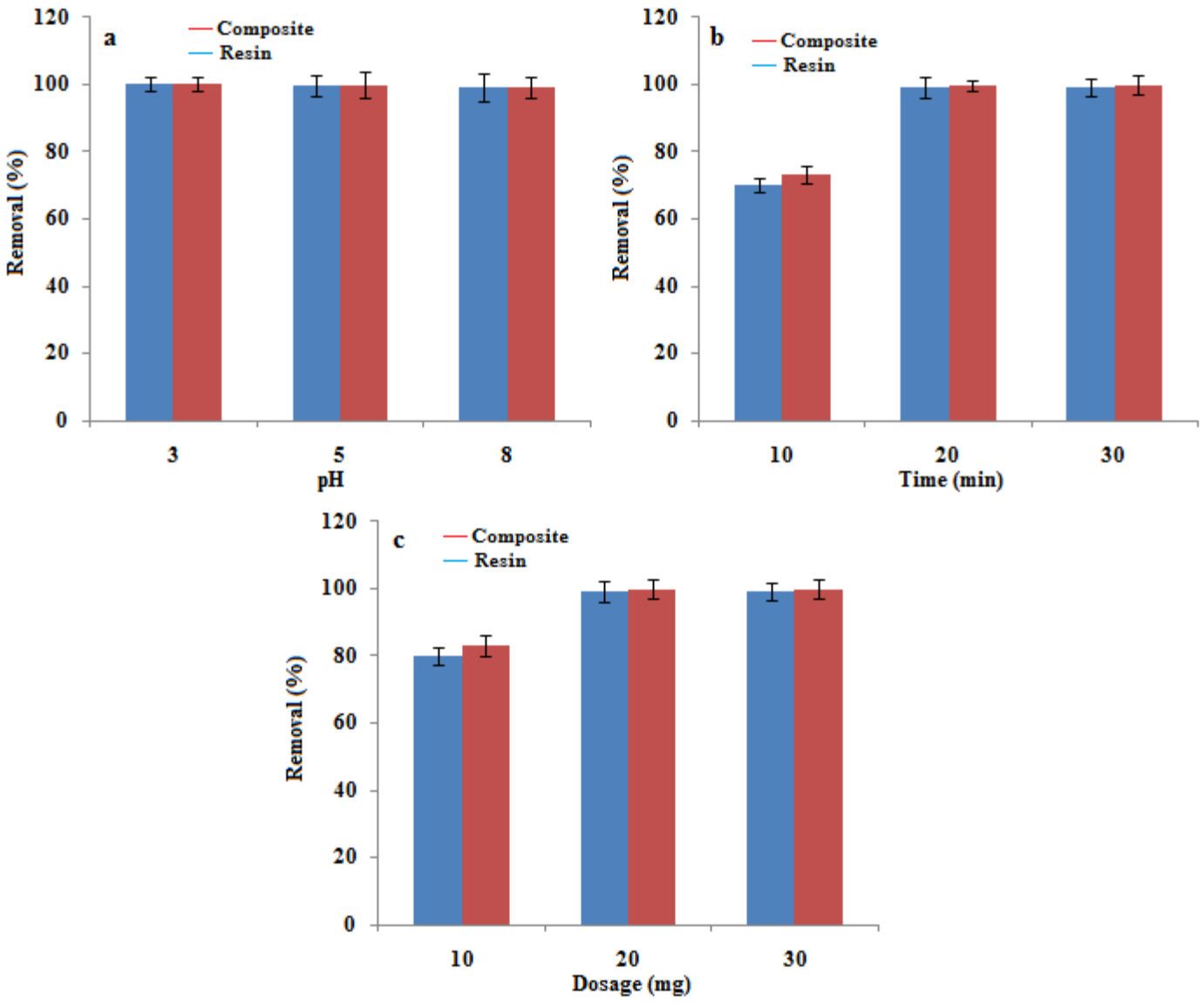

Fig.5

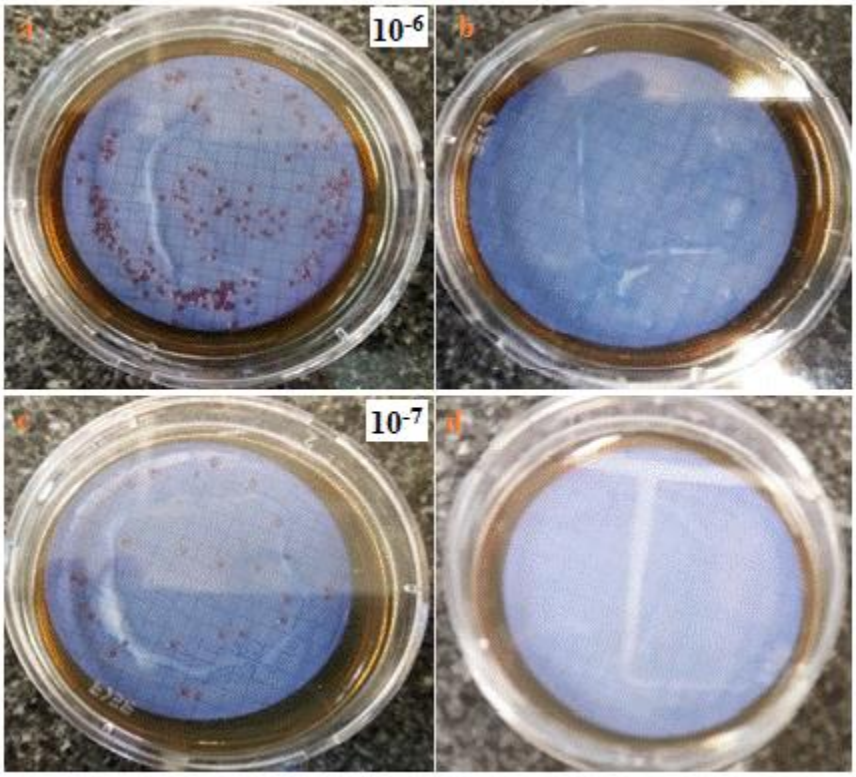

Fig.6

Table 1: BET analysis of resin and $CuFe_2O_4$@polysaccharide resin

Material	Pore diameter (nm)	a_s, BET (m^2g^{-1})	Total pore volume (cm^3g^{-1})
Resin	3.92	28.17	0.027
$CuFe_2O_4$@polysaccharide resin	5.49	13.84	0.019