




Synthesis of a Novel Composite Sorbent Coated with Siderite Nanoparticles and its Application for Remediation of Water Contaminated with Congo Red Dye

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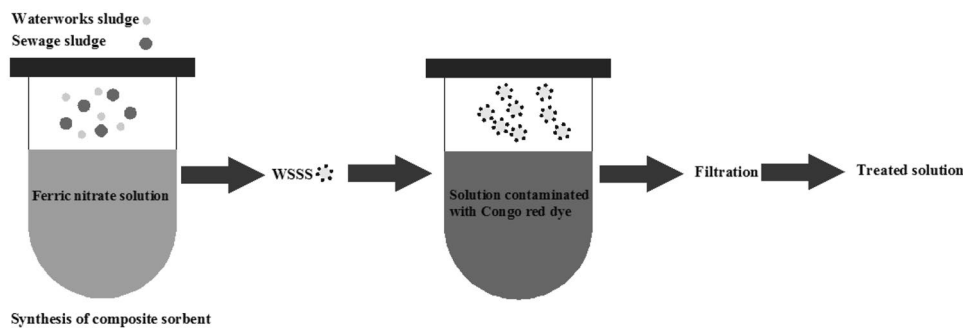
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Abstract

Re-use of the byproduct wastes resulting from different municipal and industrial activities in the reclamation of contaminated water is real application for green projects and sustainability concepts. In this direction, the synthesis of composite sorbent from the mixing of waterworks and sewage sludge coated with new nanoparticles named “siderite” (WSSS) is the novelty of this study. These particles can be precipitated from the iron(II) nitrate using waterworks sludge as alkaline agent and source of carbonate. Characterization tests using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) mapping revealed that the coating process was correctly achieved and siderite nanoparticles were planted on the surface of the composite sorbent. Interaction between Congo Red dye and composite sorbent was evaluated through a set of batch tests under the variation of agitation time, pH of aqueous solution, and sorbent dosage. The results proved that the prepared sorbent had a high ability in the treatment of water contaminated with Congo Red dye in comparison with previous studies and the maximum adsorption capacity reached to maximum value i.e. 9416 mg/g. The sorption process was governed by electrostatic attractions; however, Sips and Pseudo-second-order models described this process with coefficient of determination greater than 0.99.

Graphic abstract



Keywords Siderite nanoparticles · Modified Langmuir model · Coating · Simulation · Sorption

Introduction

The severe issues concerning anthropogenic water contamination and natural geogenic scarcity of safe water worldwide have become one of the major engineering challenges of the twenty-first century (Naushad et al. 2015a; Mironyuk et al.

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2019). More than 2000 chemical contaminants have been found in wastewater, especially organic pollutants and heavy metal ions (Ali et al. 2020; Tatarchuk et al. 2019; Naushad et al. 2016b). Among them, disposal of organic compounds arising from various industries such as cosmetics, leather, plastics, paper, pharmaceuticals and textiles industries, has attracted much attention in recent years because of those effluents (Golka et al. 2004; Bao et al. 2011; Sarkar et al. 2018; Naushad et al. 2019) contain a broad types of highly toxic and carcinogenic contaminants (Sahoo et al. 2019). Dyes with aromatic molecular structures are difficult to biodegrade into environmental-friendly substances and quite toxic on the several microorganisms (Sonal et al. 2018; Arslan-Alaton et al. 2009). Congo Red is acidic and anionic dye that can be used as an antifungal therapeutic agent in the field of aquaculture, commercial fish hatchery, and animal husbandry (Sahoo et al. 2019; Ahmad et al. 2007). It has several negative effects on the human beings such as amyloidosis (Frid et al. 2007); accordingly, Europe, United States, Canada and others prohibited the usage of this dye (Gopinathan et al. 2015). Thus, it is of paramount importance to eliminate Congo Red from wastewater.

Until now, many physical and chemical treatment methods have been applied for the removal of dyes from wastewater including coagulation and flocculation (Duan et al. 2010), biological degradation (Gopinathan et al. 2015), adsorption (Jiang et al. 2010; Naushad et al. 2016b), membrane filtration (Gürses et al. 2006), and ultra-chemical filtration (Allègre et al. 2006). Most of these methods have some technical shortcomings such as high cost, secondary pollution, and low processing capacity and have extremely limited application in separation and enrichment of Congo Red dye from contaminated aqueous solutions.

Fortunately, adsorption has been proved to be the most efficient technique compared to other methods due to its simple operation, environmental-friendly, versatile, high efficiency, etc. (Amin 2008). Furthermore, various adsorbents such as activated carbons, natural biosorbent, magnetic porous polymers, and nanofibrous materials have been applied for Congo Red dye removal (Wang and Wang 2007; Safarik et al. 2007; Sahoo et al. 2017, 2019). Nevertheless, these materials cannot fulfill the requirements for Congo Red dye treating due to low adsorption capacity, long diffusion time, or poor structural stability. Thus, it is imperative, but also challenging, to investigate advanced adsorbents that are highly capable of Congo Red dye capture and easy to fabricate (Deb et al. 2019).

Several million tons of waterworks sludge can be produced every year in Europe and this huge quantity can be increased dramatically in the future. The waterworks sludge is considered as “non-hazardous” material according to the EU legislation. This means that the waterworks sludge can be disposed to the sanitary landfills and an increase in the cost of the disposal

process was recorded in some countries. Conversely, this sludge was returned directly to the rivers in other countries and this cause a remarkable increase in the turbidity of the surface water. Another type of solid waste resulted as byproduct from municipal wastewater treatment plants is the “sewage sludge”. Due to the presence of phosphorus, nitrogen, and organic substances in the composition of this sludge, it can be used as fertilizer for improvement of soil. Al-Rostomia’s wastewater treatment plant/third extension in Baghdad/Iraq produces large quantities of sewage sludge which is collected in fourteen units of drying beds with apparent volume not less than 850 m³ for each unit and these quantities may be banished to the ecosystem. Hence, water companies and other authorities directed their efforts to find the cheaper solutions for minimizing the problems accompanied with the elimination of (waterworks and sewage) sludge (Basibuyuk and Kalat 2004).

Accordingly, the novelty of the present study can be summarized as follows; (1) the use of the described byproducts as sorbents could be a good solution for huge quantities of these wastes in terms of sustainable development and green projects, as well as a means of cutting disposal costs, (2) the manufacturing of nanoparticles named scientifically as “siderite” from waterworks sludge as alkaline agent with aid of Iron(II) nitrate by the new preparation method which was not adopted previously in the related topics and, (3) producing reactive material with new additional sites by planted “siderite” onto the waterworks-sewage sludge. The ability of composite material in the treatment of the wastewater was evaluated using Congo Red as target contaminant.

Herein, the waterworks sludge modified by Fe²⁺ composite was synthesized by a simple precipitation method for Congo Red removal. SEM, XRD, and EDS were applied to systematically analyze the morphologies and physicochemical properties. The influencing various factors, including temperature, contact time, solid content, pH value, ionic strength, and starting concentration, for Congo Red removal were investigated by batch experiments. Furthermore, the mechanism between WSSS and Congo Red is also studied and this paper offered new horizons for Congo Red removal from contaminated water and extended the applications of the WSSS adsorbents for environmental pollution control.

Material and Methods

Sorbent and Contaminant

Al-Wehda water treatment plant (WTP) in the Baghdad city, capital of Iraq was the source of the waterworks sludge used in the present study. The raw water entered to this plant always purified using alum salts and this means that the aluminum is definitely present in the composition of this sludge. Air was used to dry the collected sludge for three

days and, then, grinded to obtain the mesh size ranged from 1 to 0.063 mm with mean diameter of 0.25 mm (Mathews and Zayas 1989). Also, sewage sludge was collected from Al-Rostomia'a wastewater treatment plant/Baghdad/Iraq and dried at the atmospheric temperature for 5 days. Distilled water was used in the washing of the sewage sludge; then, sieving to obtain the same mesh size range as in the waterworks sludge and, finally, dried it at 70 °C for 6 h. Concentrations of heavy metals were measured in the solid phase of sewage sludge and the values are listed in Table 1 in comparison with the acceptable limits of the New Dutch list. It seems that this sludge tends to retain the heavy metals, thereby eliminating the environmental pollution (Doke et al. 2012; Simantiraki et al. 2013).

Congo Red (Central Drug House (P) Ltd.) was taken as a target contaminant for representation the aqueous solution contaminated with organic compound. To simulate the water's Congo Red contamination, a solution of Congo Red was prepared with concentration of 1000 mg/L and it was kept at room temperature. Successive dilutions for this solution were adopted to prepare the required concentration of Congo Red and 0.1 M HCl (or 0.1 M NaOH) was added to adjust the pH of the solution.

Preparation of Composite Sorbent

A modified precipitation method was adopted where different percentages of waterworks sludge/sewage sludge were added to 50 mL of solution containing 2 g $\text{Fe}(\text{NO}_3)_2$. To specify the best percentage of these two sludge, the mixture was stirred for 180 min using orbital shaker, dried at 105 °C for 4 h and, then, washed with de-ionized water to remove unattached nanoparticle. After that, the best percentage was added to different concentrations of $\text{Fe}(\text{NO}_3)_2$ solution and the mixture was stirred and dried in the same procedure mentioned previously. In the final step, the solid particles were dried at 105 °C for 24 h and stored in a capped bottle for further use (Phuengprasop et al. 2011). The adsorption capacity for Congo Red dye using the composite sorbents coated with nanoparticles of siderite prepared under different preparation conditions was the main criterion used in

Table 1 Measured concentrations of heavy metals in the solid phase of the sewage sludge

Metal	Concentration (mg/kg)	New Dutch limits (Doke et al. 2012)
Cadmium	<0.5	12
Copper	100	190
Lead	32	85
Nickel	30	210
Zinc	450	720

the evaluation of the best sorbent. Surface morphology of waterworks sludge, sewage sludge, and prepared composite sorbent coated with siderite nanoparticles was examined by scanning electron microscopy (SEM) equipped with an EDS (XFlash 5010; Bruker AXS Microanalysis, Berlin, Germany). Digital mapping can be generated from EDS analysis for adopted sorbents where the brightness of the images is correlated with the intensity of the pixels for the elements in the sample. Crystalline structures of different sorbents described previously were examined via X-ray diffraction (XRD) analysis at wavelength (λ) of 1.789 Å (Siemens X-ray diffractometer, D8 Advance, Bruker, Germany) in Germany Laboratory/Department of Geology/University of Baghdad.

Sorption Tests

Here, 250 mL conical-flasks were taken and 50 mL of aqueous solution contaminated with 50 mg/L of Congo Red dye was added to each flask. Different dosages of sludge ranged from 0.01 to 0.3 g were added to each flask and the mixture was kept stirred on an agitation speed equal to 200 rpm using orbital shaker (Edmund Buhler SM25, German). To separate solid phase from liquid phase, treated aqueous solution was filtered using filter paper type (JIAO JIE 102) and certain volume (≈ 10 mL) of filtered solution was analyzed to measure the concentration of Congo Red using an ultraviolet–visible (UV) spectrophotometer (Shimadzu Model: UV/VIS-1650) at the maximum absorption wavelength of 497 nm. The experiments for specifying the equilibrium time were implemented by withdrawing the periodic samples through the time period not exceeding 300 min. Additional tests were conducted to study the effect of initial pH in the range of (3–9.6) on the removal efficiency of Congo Red with constant concentration of Congo Red (1000 mg/L). The removal efficiency of the contaminant was calculated as follows:

$$R = \frac{(C_o - C_e)}{C_o} \times 100, \quad (1)$$

where C_o and C_e are the initial and equilibrium concentrations of Congo Red dye (mg/L). The amount of this contaminant retained in the sorbent material, q_e (mg/g), was determined as:

$$q_e = (C_o - C_e) \frac{V}{m}, \quad (2)$$

where m is the sorbent quantity that added to the flask (g) and V is the volume of aqueous solution (L).

Sorption Models

The sorption models describe the specific relation between sorbed quantity of dye onto solid phase (q_e) and the concentration of dye in the bulk solution (C_e) at equilibrium state (Zheng et al. 2009). This relation can be represented by Freundlich, Langmuir and Sips models (Table 2) and these models are plotted at constant values of pH and temperature. In addition, it is important to predict the rate at which dye removed from aqueous solutions to design appropriate sorption treatment processes (Puranik et al. 1999), accordingly, the sorption kinetic models (Lagergren 1989; Ho and McKay 1999; Ho et al. 2002; Hamdaoui and Naffrechoux 2007; Gheju and Miulescu 2007; Foo and Hameed 2010) mentioned in the Table 2 can be used to find this rate.

Results and Discussion

Composite Sorbent

Composite sorbent adopted in the present study is a mixture of waterworks sludge and sewage sludge treated with different amounts of Iron(II) nitrate to achieve the required coating by precipitation of the nanoparticle materials. The maximum sorption capacities were determined due to the interaction of Congo Red dye with different percentages of composite sorbent under various quantities of Iron(II) nitrate as shown in Fig. 1. It is clear that the increase of waterworks sludge amount from 0 to 0.75 g/g caused a significant increase in the sorption capacity. This might be due to the dissolution of calcium carbonate (the main constituent of waterworks sludge) in the aqueous solution where the calcium ions increased the pH and,

consequently, this led to precipitate a new nanoparticles named as siderite on the composite sorbent. The reactions governing the precipitation process is described by the following equations:



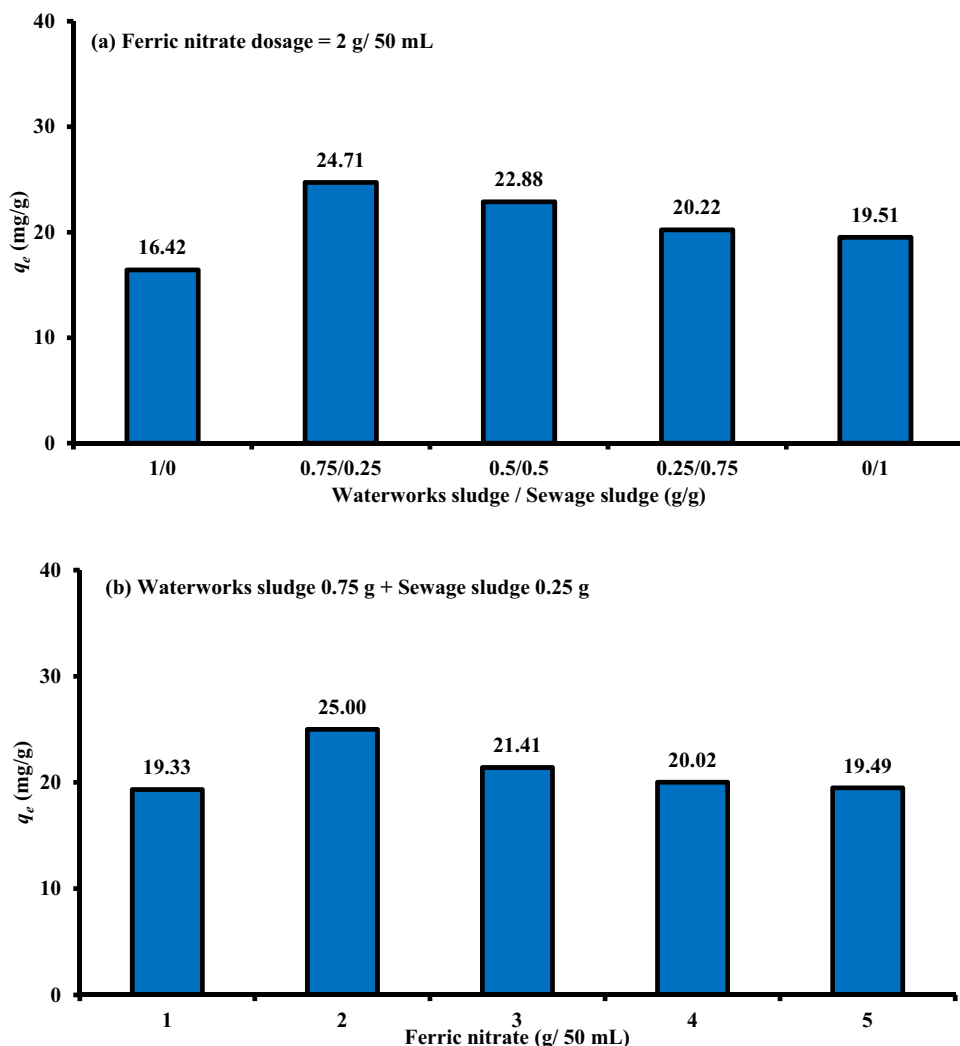
When the waterworks sludge quantity was equal to 0.75 g of composite sorbent, the coating with siderite increased the sorption capacity up to 24.7 mg/g in comparison with capacity value that was equal to 19.5 mg/g for composite sorbent consisted of sewage sludge only. This means that 0.75 g waterworks sludge mixed with 0.25 g sewage sludge represented the best mixture used to prepare a composite sorbent coated with siderite nanoparticles. To specify the better quantity of Iron(II) nitrate that used in the coating process, the best mixture of composite sorbent was treated with different amounts of this nitrate in the range of (1–5 g) added to 50 mL of aqueous solution. Figure 1b shows the effect of Iron(II) nitrate dosage on the sorption capacity of Congo Red on the coated composite sorbent. The results certified that the increase of Iron(II) nitrate from 1 to 2 g caused a significant increment in the sorption capacity and this capacity was decreased beyond 2 g. This reduction may be due to the saturation of surface area on the composite sorbent with siderite particles and excessive amount of these particles (i.e. uncoated siderite) would be removed by washing at the end of preparation process, therefore, 2 g of Iron(II) nitrate will be adopted coating.

Table 2 Isotherm and kinetic models used to describe the sorption data

Model	Formula ^a	References
Isotherm		
Freundlich	$q_e = K_F C_e^{1/n}$	Deb et al. (2019) and Ho et al. (2002)
Langmuir	$q_e = \frac{q_{max} b C_e}{1 + b C_e}$	Foo and Hameed (2010)
Sips	$q_e = \frac{K_s C_e^{\beta_s}}{a_s C_e^{\beta_s} + 1}$	Hamdaoui and Naffrechoux (2007)
Kinetic		
Pseudo first order	$q_t = q_e [1 - \exp(-k_1 t)]$	Lagergren (1989)
Pseudo second order	$q_t = k_2 q_e^2 t / (1 + k_2 q_e t)$	Ho and McKay (1999)

^a K_F is related with the adsorption capacity of the sorbent, and n is the intensity of sorption; q_{max} is the maximum adsorption capacity (mg/g), and b is the affinity between the dye and sorbent; K_s , a_s and β_s are the constants; k_1 is the equilibrium rate constant of pseudo first order sorption (1/min), k_2 is the rate constant of sorption (g/mg min), q_e is the quantity of dye sorbed at equilibrium (mg/g), and q_t is the quantity of dye sorbed at time t (mg/g)

Fig. 1 Sorption capacity of Congo Red dye onto composite sorbent under the effects of different **a** ratios of waterworks sludge mixed with sewage sludge and **b** dosages of ferric nitrate



Characterization of Different Sorbents

Figure 2 shows the crystalline structures for waterworks sludge, sewage sludge, and prepared composite sorbent coated with siderite nanoparticles through plotting the patterns of the X-ray diffraction (XRD) analysis. It is clear that the silica oxide, calcite, and iron oxide are the main components of waterworks sludge, however, the hydroxyapatite and iron oxide can be recognized in the composition of the sewage sludge. Also, this figure certifies that the coating of the prepared composite sorbent with siderite nanoparticles is achieved in the efficient manner depended on the peaks of (24.8, 32.1 and 38.4) with Miller planes of (012, 104, and 110).

Figure 3 elucidates the morphology of waterworks sludge, sewage sludge, and prepared composite sorbent coated with siderite nanoparticles using SEM images. It seems that the shape of these sorbents before interaction with Congo Red dye is irregular with evidence pores, however, nanoparticles of the siderite can be attached on the surface of composite

sorbent after sorption process. Multi-elemental EDS mapping images for same sorbents before and after sorption process signified the presence of C, O, Mg, Na, Al, Fe, N, Ca, Si, Ti, N, S and P constituents as shown in Fig. 4. The maps corresponding for these peaks revealed that there are bright spots for the calcified area with heterogeneous distribution of the elements in the view of the cross-section. This figure illustrates the increase of Fe intensities in the green dotted areas for composite sorbent and this related with the presence of siderite nanoparticles or, in other words, the success of coating process. In addition, the increase of S intensities in the pink dotted areas after sorption process means the removal of Congo Red dye on the coated sorbent.

Contact Time

The contact time required to achieve the equilibrium status must be specified and the effect of contact time on the removal of Congo Red dye using 0.05, 0.08, 0.1, 0.3 and 0.5 g of composite sorbent added to 50 mL of aqueous

Fig. 2 XRD patterns of the waterworks sludge, sewage sludge, and composite sorbent before sorption process

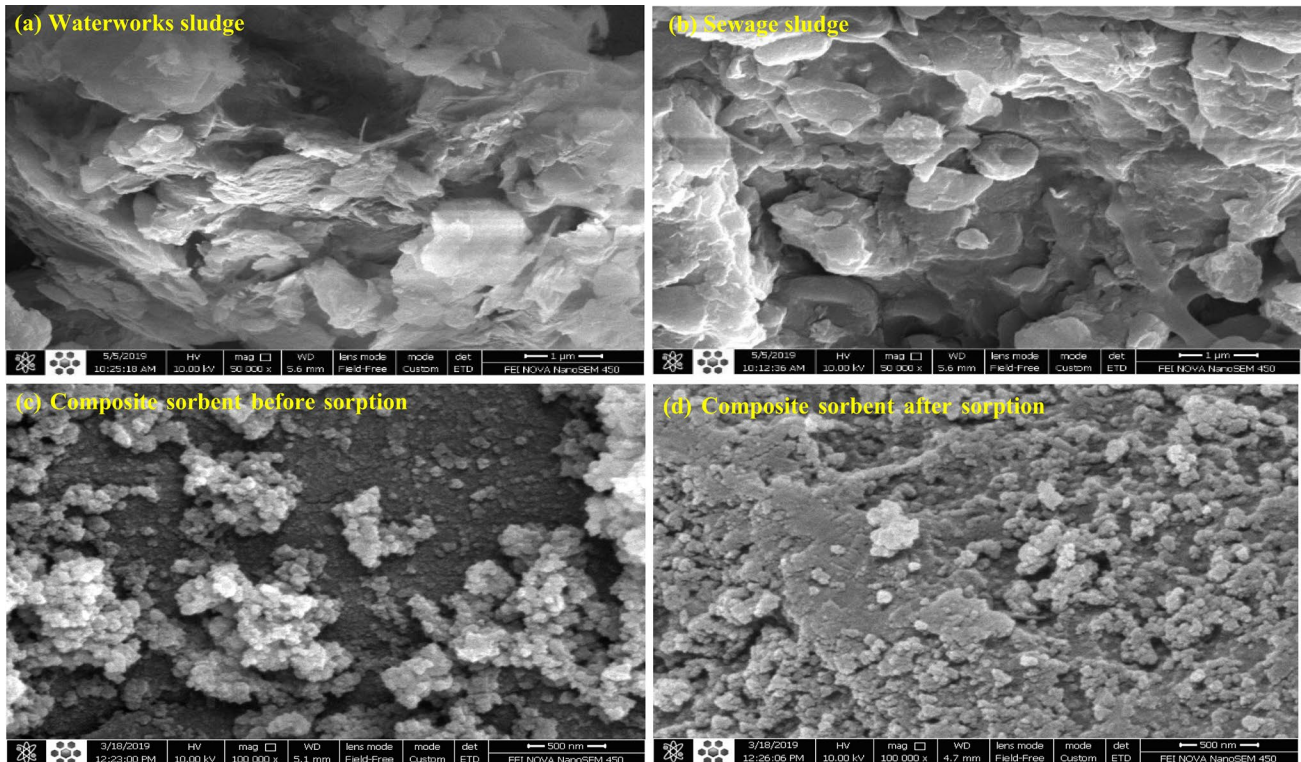
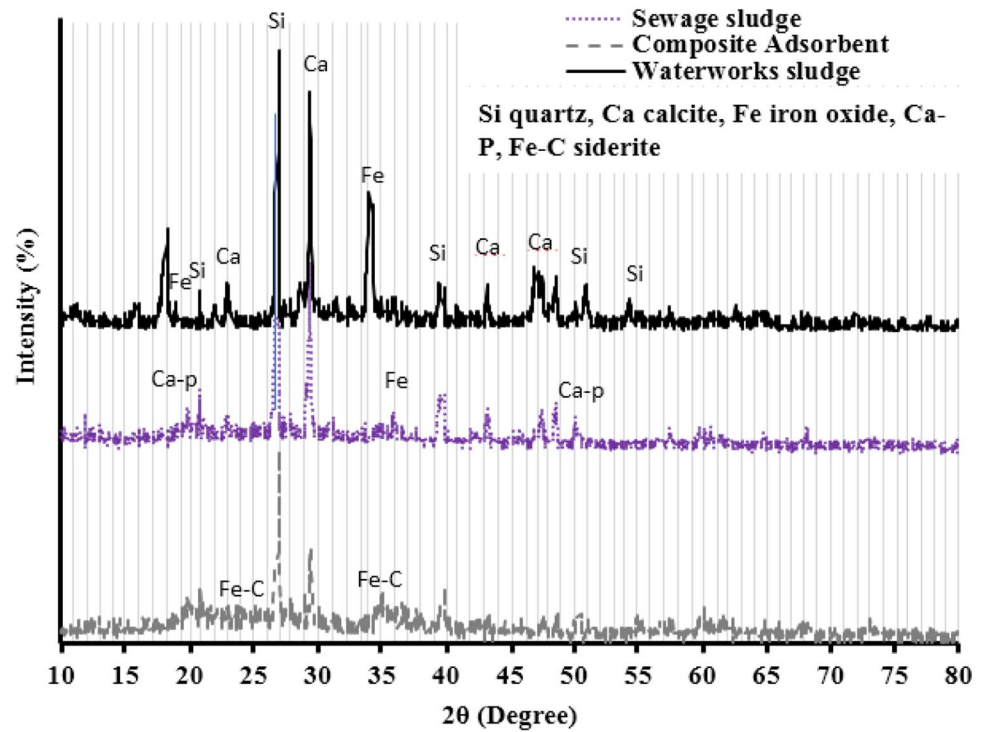


Fig. 3 Scanning electron microscopy (SEM) images of waterworks sludge, sewage sludge, and composite sorbent used in the present study

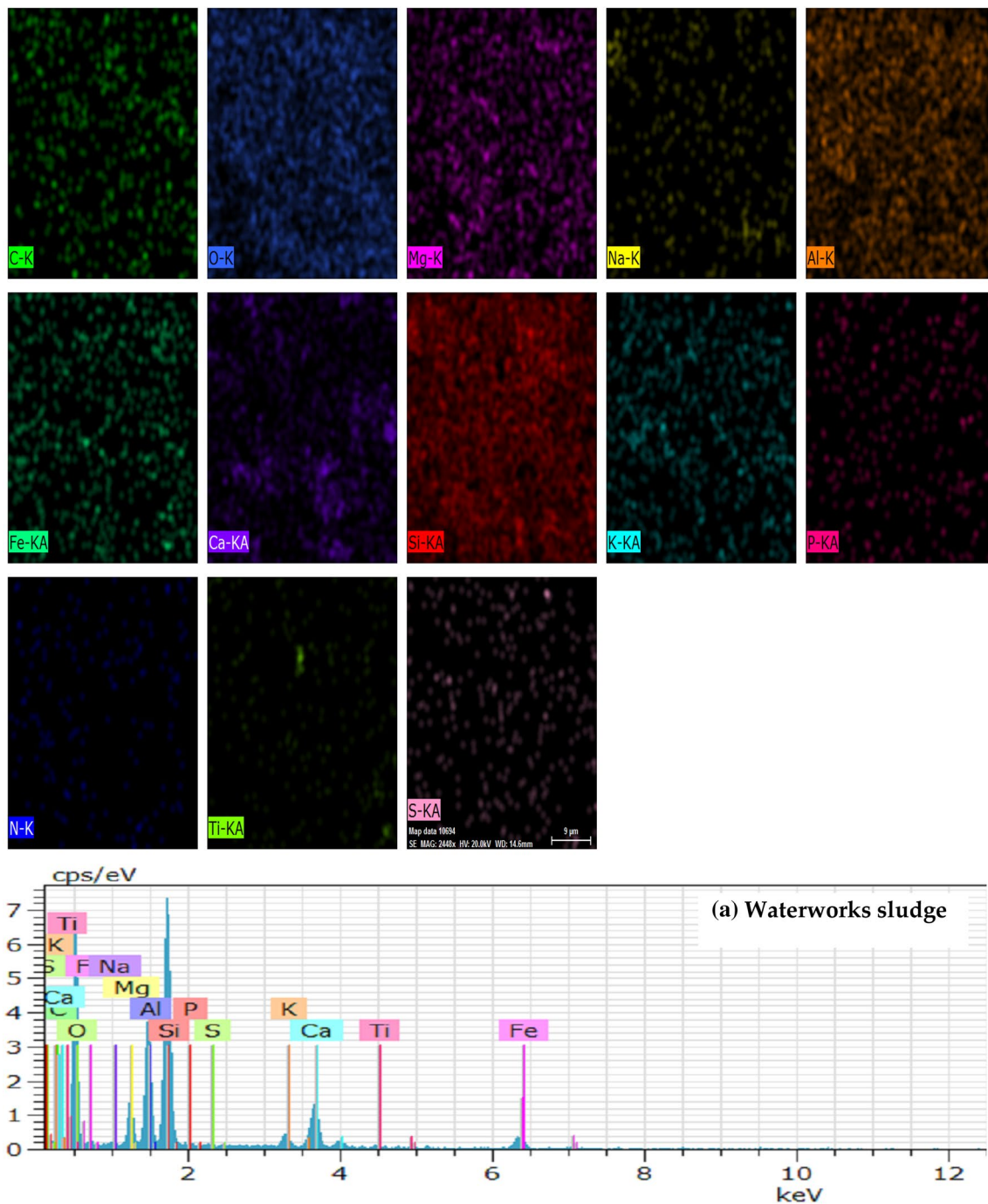


Fig. 4 EDS and EDS mapping of waterworks sludge, sewage sludge, and composite sorbent used in the present study

solution at room temperature and initial concentration of 50 mg/L is plotted in Fig. 5a. This figure demonstrates that the increase of contact time has a positive effect on the removal percentage of the target contaminant. In the initial stages, the sorption rate was incremental increase and, afterwards, it can be gradually slowed. This reduction in

the rate of the sorption definitely related with decrease of the vacant sites on the surface of the sorbent. The kinetic data shows that 71% of Congo Red dye was removed mainly at 5 min with sorbent dosage of 0.05 g/ 50 mL and there was no significant change in residual concentrations after this equilibrium time up to 270 min.

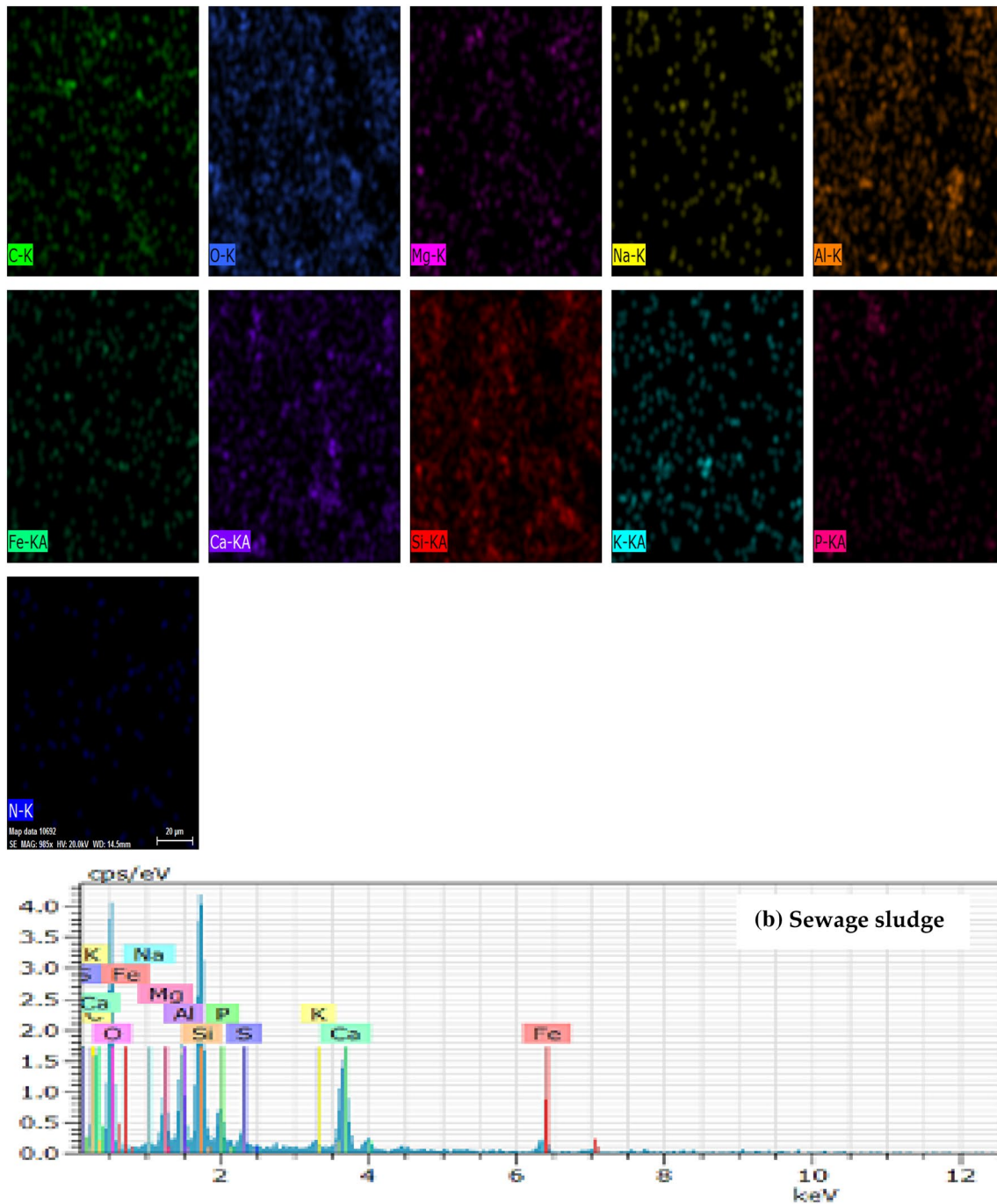


Fig. 4 (continued)

Initial pH of Contaminated Water

The effect of pH on the removal of Congo Red dye from aqueous solution was studied in the range from 3 to 9.6 (Fig. 5b). At pH of 7, the color of the dye was red and it remains the same at alkaline solution (i.e. pH > 7); however, dark blue color was recognized for acidic solution (i.e. pH < 5). Also, it is observed that the solubility of dye

was decreased at pH less than 2 and, consequently, the lowest value of pH adopted in the tests was 3.1 (Sahoo et al. 2019). The maximum removal efficiency of Congo Red dye was recorded at pH of 3.1 with value of 100% and this removal was approximately remained constant until pH equal to 6, however, gradually decrease in the removal efficiency was recognized with increase of initial pH to reach the value of 50% at pH equal to 9.6. For pH equal to

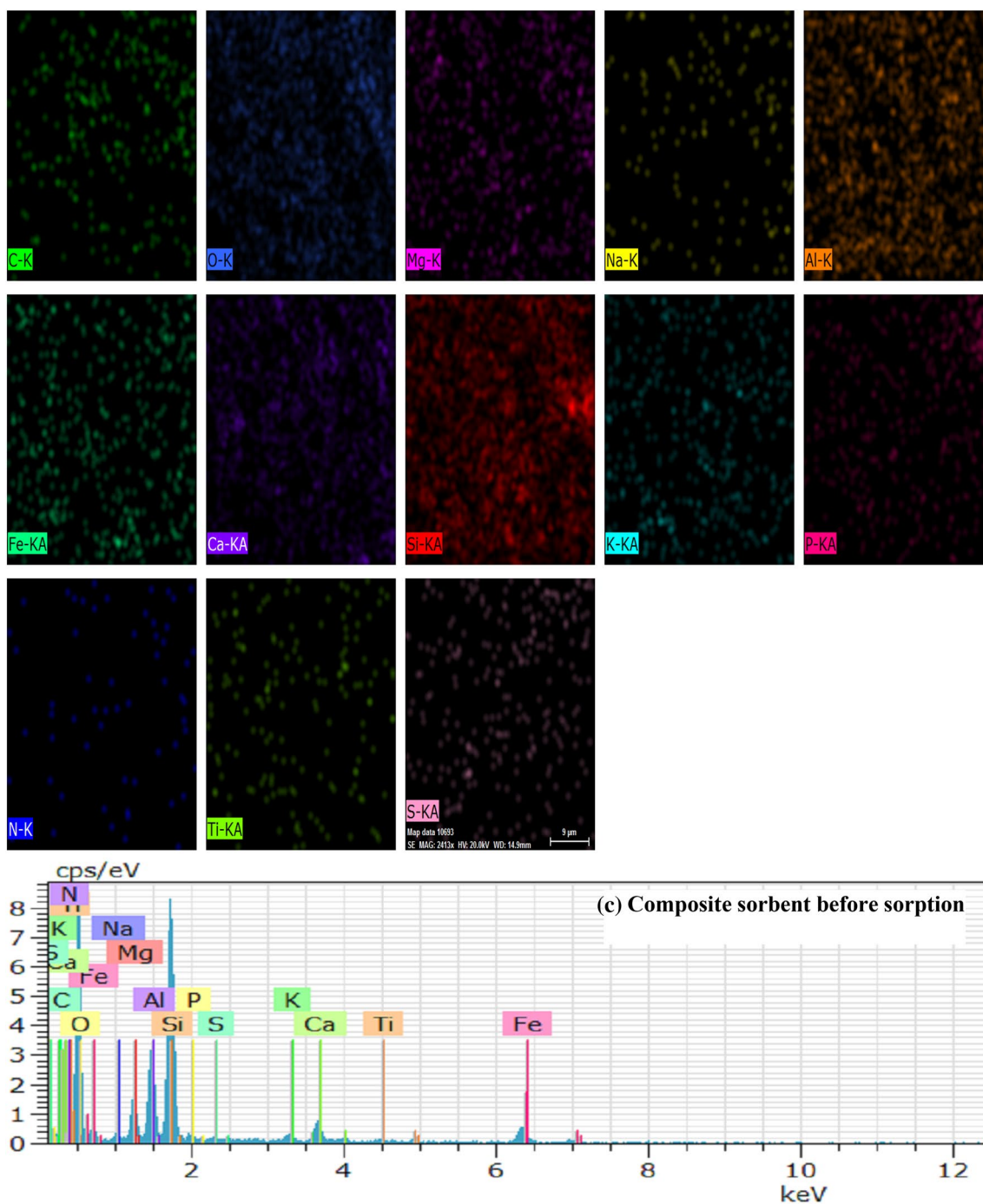


Fig. 4 (continued)

3.1, a strong interaction can be generated between anionic dye and positive charge surface of sorbent due to electrostatic attraction. Conversely, electrostatic repulsion can be appeared at higher pH between anionic dye and the negative charges on the surface sites. Also, a competition between excess of OH⁻ ions and anionic dye on the bonding sites can be explained the decrease of removal

efficiency in the basic solution. The same results were recorded for the sorption of Congo Red dye on dialdehyde cellulose-cross linked cellulose-chitosan foam (Kim et al. 2019), graphene oxide-NiFe layered double hydroxide (Zheng et al. 2019) and amine functionalized magnetic iron oxide nanoparticles (Sahoo et al. 2019).

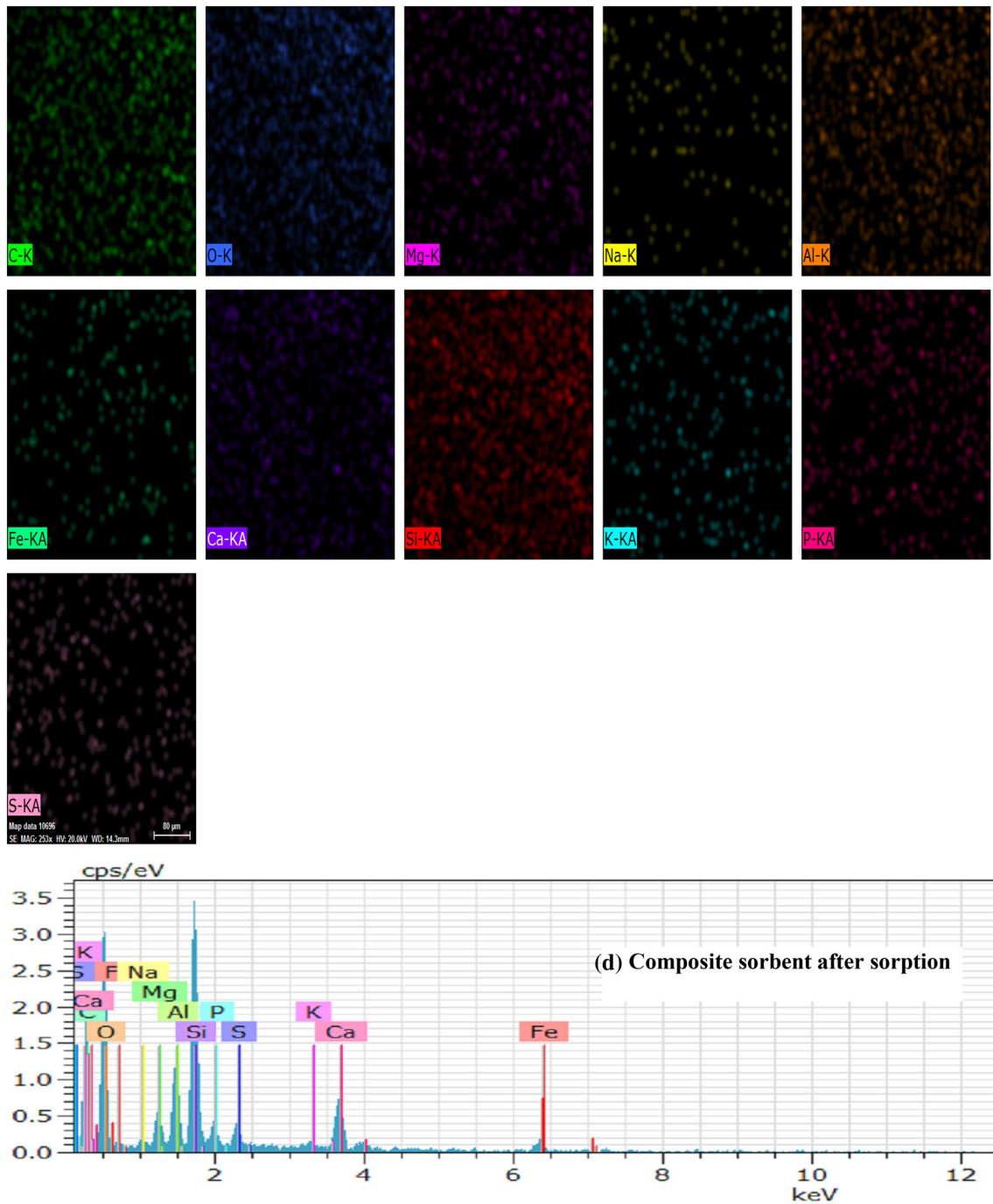


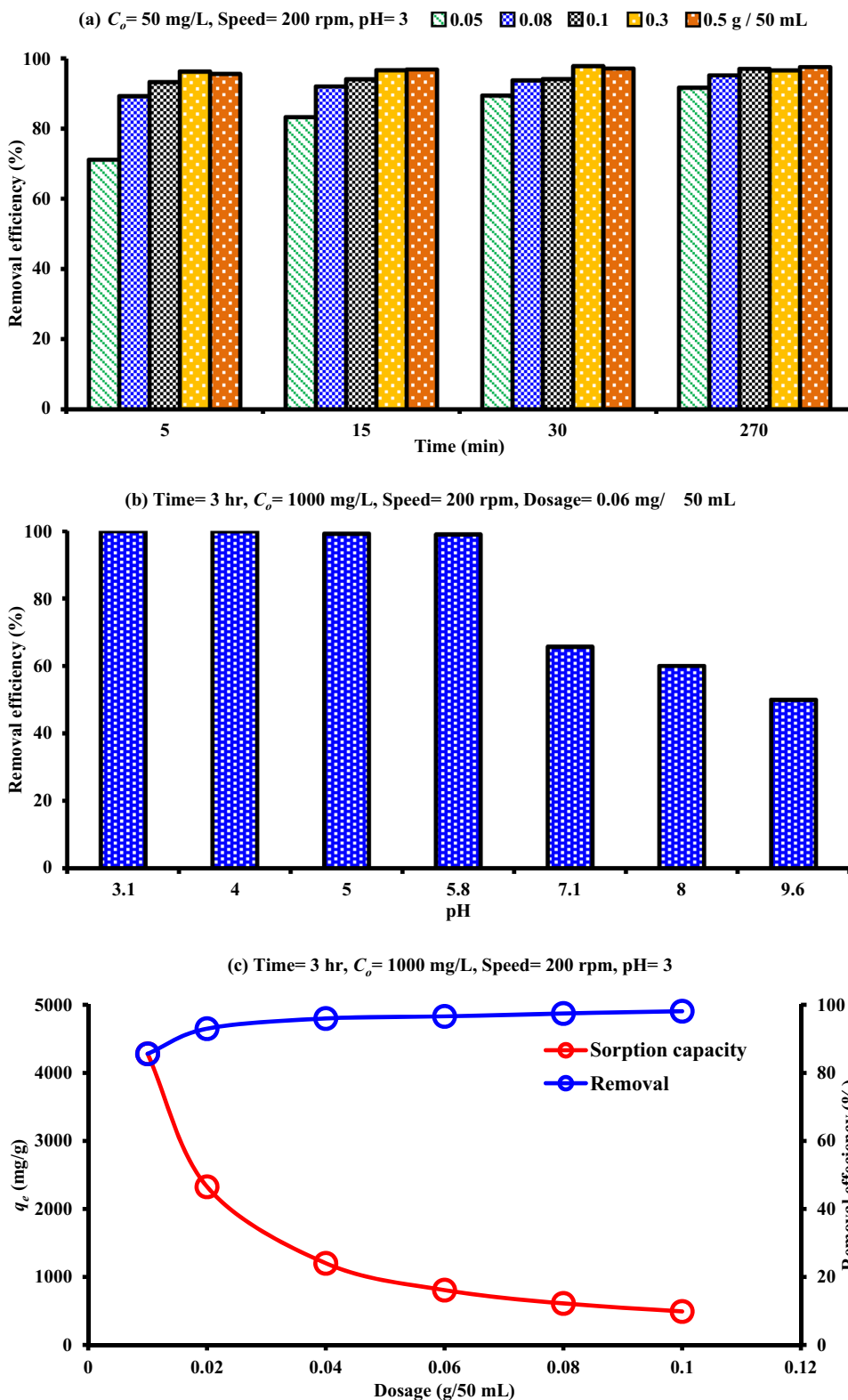
Fig. 4 (continued)

Dosage of Composite Sorbent

Sorbent dosage significantly affected the removal efficiency of contaminant species. This parameter was investigated at room temperature by changing the amounts of composite sorbent from 0.01 to 0.1 g (Fig. 5c) added to

50 mL of contaminated water where the dye concentration of 1000 mg/L, pH of 3 and equilibrium time of 3 h. It is clear that the increasing of sorbent dosage enhanced the dye removal efficiency until it reached the steady state trend, however, this will be accompanied by a significant reduction in the sorption capacity.

Fig. 5 The effect of various operation conditions on the sorption of Congo Red dye onto the prepared composite sorbent

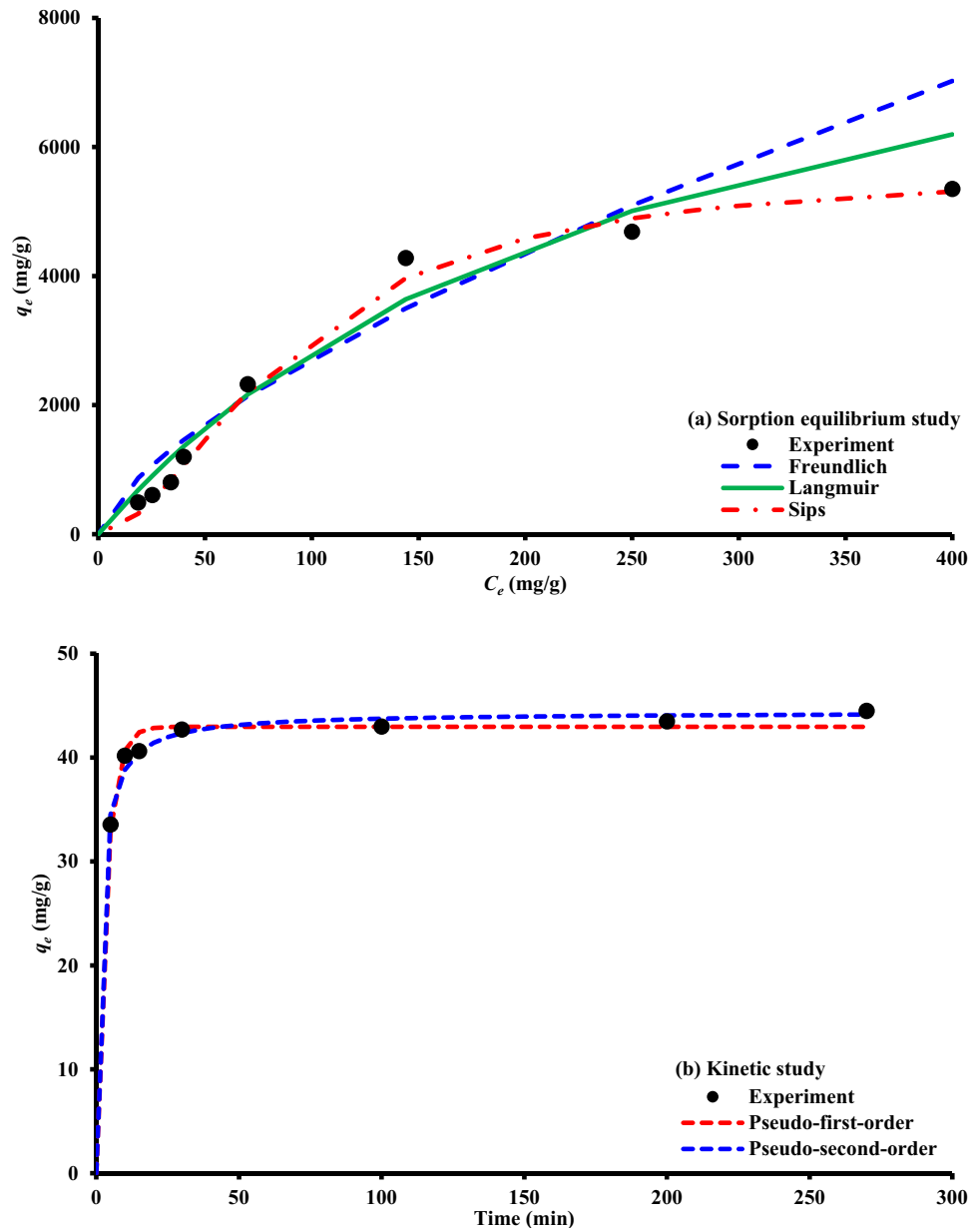


Isotherm and Kinetic Models

Freundlich, Langmuir and Sips isotherms are shown graphically in Fig. 6 where their constants are listed in Table 2

which were determined by fitting with measured data using “Solver” option for nonlinear expressions in Excel 2016. It is clear that all models presented a good representation for experimental measurements, however, Sips model was more

Fig. 6 Isotherms and kinetics models used in the present study



representative for fitted data from other models because the value of determination coefficient (R^2) equal to 0.997 as given in Table 3. The application of Sips model means that the sorption process was heterogeneous. The most important character of the prepared composite sorbent was its high maximum sorption capacity which was 9416 mg/g as illustrated in Table 3. This value was greater than the findings of the previous studies (Yang et al. 2015; Zheng et al. 2017, 2019; Zhao et al. 2017; Bao et al. 2019) as shown in the Table 4 and, accordingly, the present composite sorbent coated with siderite nanoparticles manufactured from byproduct wastes can be used as substitute option for many industrial sorbents. In addition, the nonlinear fits for the kinetics results using kinetic models proved that the Pseudo

second order model exhibits higher R^2 and lower value of sum of squared errors (SSE) in comparison with the Pseudo first order model (Fig. 6 and Table 3). This specifies that the sorption kinetics process follows Pseudo second order and this process was governed by chemisorption mechanism which involved valence forces between dye anion and composite sorbent.

Possible Mechanisms

Removal of Congo Red dye could be probably achieved by two possible mechanisms namely; (1) electrostatic interaction between the protonated groups of nanoparticle or organic functional groups of sewage sludge and acidic

Table 3 Constants of the isotherm and kinetic models specified from non-linear regression analysis for Congo Red dye sorption onto composite sorbent

Constants of models	Value
Freundlich	
K_F	118.17
n	1.467
R^2	0.937
Langmuir	
q_{max}	9416
b	0.0045
R^2	0.968
Sips	
K_s	1.722
β_s	1.7995
a_s	0.0003
R^2	0.997
Pseudo-first-order	
k_1	0.293
q_e	42.967
SSE	6.4615
R^2	0.922
Pseudo-second-order	
k_2	0.0158
q_e	44.369
SSE	3.9321
R^2	0.952

Table 4 Maximum sorption capacities for prepared composite sorbent in comparison with different reactive materials adopted from previous studies for Congo Red dye as target contaminant

Material	q_{max} (mg/g)	References
Composite sorbent	9416	Present study
3D hierarchical GO-NiFe LDH	489	Zheng et al. (2019)
Flower-Like NiO microspheres	534.8	Zheng et al. (2017)
Core-shell Fe(OH) ₃ @Cellulose	689.65	Zhao et al. (2017)
NiCo ₂ O ₄ nanosheets	961.5	Bao et al. (2019)
CNT/Mg(Al)O nanocomposites	1250	Yang et al. (2015)

dye and (2) the chemical reaction between the dye and the composite sorbent. At low pH, high electrostatic attraction exists between the anionic dye and positively charged surface of the solid particles. With increase of pH, an increase in the number of negatively charged sites can be observed and, accordingly, these sites don't favor the adsorption of dye anions due to the electrostatic repulsion. Also, lower adsorption of Congo Red dye at alkaline system may be due to the presence of excess hydroxides ions competing with the dye anions for the adsorption sites. However, significant adsorption of the anionic dye on the adsorbent still occurred at alkaline pH. This suggested that the second mechanism,

i.e. chemisorption, might be operative. A similar trend was observed for the adsorption of Congo Red on materials like biogas residual slurry as well as waste orange peel and banana pith (Namasivayam and Kavitha 2002; Bhowmik et al. 2018a, b).

Regeneration Study

Desorption study aims to express the nature of adsorption, ability for recycling of the spent adsorbent with recovery of Congo Red dye. The desorption process was performed by mixing of spent adsorbent with 0.01 mol/L of NaOH solution and the desorption efficiency was found greater than 96%. This means that Congo Red dye could be desorbed from the loaded adsorbent by changing the pH of the solution to the alkaline range and NaOH solution has higher desorption efficiency.

Conclusions

The unique property of this study was to synthesize a new composite sorbent consisted of the mixture of byproduct wastes (waterworks sludge and sewage sludge) coated with siderite nanoparticles and the results proved that this sorbent had an excellent ability in the removal of Congo Red dye from simulated wastewater. The siderite nanoparticles were prepared from the precipitation of Iron(II) nitrate using waterworks sludge as alkaline agent and source of carbonate. Characterization tests such as XRD, SEM, and EDS mapping elucidated that the coating process led to produce the efficient sorbent with maximum sorption capacity arrived to 9416 mg/g and this can be attributed to nanoparticles (i.e. new sites) planted on the composite material. In comparison with Freundlich and Langmuir isotherm models, the sorption of Congo Red dye onto the prepared composite sorbent was described well by the Sips heterogeneous model with R^2 not less than 0.997, while the sorption kinetic was represented by Pseudo-second-order expression. The authors recommend to study the ability of using the prepared composite sorbent in the future studies for fixed bed column or for the permeable reactive barrier technology to restriction and containment of the contaminant front and finding the longevity of the bed that satisfied the environmental regulations.

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