Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2023.29540

293 (2023) 208–215
May

Removal of Cd(II) ion from aqueous solution using magnetic ionic liquid based nanocomposites [$NiFe_2O_4$@BMSI]Br: kinetics, isotherm and thermodynamic studies

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Received 17 March 2023; Accepted 6 April 2023

ABSTRACT

The pollution of soil and water recourses by toxic metals is a serious global problem, and it is challenging to eradicate their long-standing effects. Several techniques have been widely used for water treatment. Among all available techniques, adsorption is one of the most promising techniques for the treatment of wastewater due to its simplicity of design, ease of operation and no secondary pollution. The current study presents the results of adsorption studies on Cd(II) removal from aqueous solution using a magnetic ionic liquid based nanocomposites [$NiFe_2O_4$@BMSI]Br. The optimum pH was noted 7 and equilibrium was attained within 180 min. The experimental equilibrium data for Cd(II) adsorption using [$NiFe_2O_4$@BMSI]Br nanocomposite was well fitted to the pseudo-first-order kinetic and Langmuir isotherm models. Thermodynamic studies showed that Cd(II) adsorption using [$NiFe_2O_4$@BMSI]Br was endothermic and spontaneous process.

Keywords: Ionic liquid; Toxic metal; Cd(II); Adsorption

1. Introduction

The clean water is outmost necessity in present times in every sphere of life either it is agriculture, industry or for human consumption [1,2]. Thus wastewater treatment, water management and reusability are of immense importance [2,3]. The growing population has put enormous pressure on water resources leading to their depletion and pollution. Numerous contaminates were added to the water bodies which includes dyes, agrochemicals, pharmaceuticals products and heavy metal ions etc [4–6]. Heavy metals such as arsenic, cadmium, lead, zinc, cobalt, copper, titanium, lithium, mercury and aluminum exist in the form of metals or dissolved salts [7,8]. The remediation of these metal ions can be carried out using various processes such as ion-exchange, adsorption, electrocoagulation, osmosis, membrane filtration and solvent extraction [9–12]. The adsorption related decontamination technologies is the common approach for segregation and exclusion of toxic metals from polluted water [13–15]. For the adsorption processes, the utmost dire feature is the selection or designing of capable and appropriate adsorbents with very high adsorption capability and easy-to-recycle assets [16,17]. Development of regenerable and competent heavy metal ion adsorbent materials is extremely necessary for wastewater remediation, for retrieval of precious metals and desalination etc [18]. In this context, various adsorbents materials have been researched for the removal of different types of heavy metal ions which incudes, polymers, activated carbon, zeolites, clays, metal organic frame works, carbon nanotubes, MXenes, organic and inorganic ion exchangers, carbon nitride and graphene etc [19–22]. Though, these adsorbents face poor binding affinities, reduced selectivity and low efficiency etc. Therefore, alternative adsorbents need to be

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researched and checked for their potential adsorption efficiency [23,24]. The fabrication of ionic liquids has opened a new class of adsorbent materials with better selectivity and good adsorption efficiency [25]. The numerous magnetic and non-magnetic ionic liquids have been developed and used as adsorbents for toxic metals removal [26,27]. For example, ionic liquid filled chitosan capsules has been investigated for Cr(VI) removal from acidic medium [28]. Wang et al. [29] grafted ILs at MXenes' surface and introduced into the solution of NIPAM monomer to achieve composite hydrogels which improved the adsorption capacity and mechanical strength of the composite hydrogel. It's q_m for 4-nitrophenol was noted to be 200.29 mg/g. Firmansyah et al. [30] impregnated a phosphonium-based IL, trioctyldodecyl phosphonium bromide (P8,8,8,12Br) on mesostructured silica nanoparticle for adsorptive removal of lead metal ions. Even in some studies the ionic liquids have been used for functionalization of adsorbents which improved their adsorption capacity. The chitosan beads were bi-functionalized with the IL (Aliquat 336) and CTAB and potentially used for remediation of tartrazine [31]. Yılmazoğlu et al. [32] modified the montmorillonite clay by means of ILs N-butylimidazolium tetrafluoroborate (BIM) and N-methylimidazolium tetrafluoroborate (MIM) [32]. The IL modified MMT clays demonstrated better adsorption efficiency for the exclusion of orange II anionic dye from aqueous medium. The imidazolium-based poly(ionic liquids) (PILs) have been considered as promising aspirant for remediation of valuable metal ions [33]. Wu et al. [34] fabricated two magnetic graphene oxide composites, specifically with ionic liquids and studied various IL-functional group substitution contents on the β-cyclodextrin (β-CD). The above composites were successful explored for their adsorption nature for anionic dyes. Similarly, composite of ionic liquids and cellulose nanocrystals was prepared with date pits to have a low-cost and eco-friendly material for lithium removal [35]. Shang et al. [36] prepared a novel composite of graphene oxide-dicationic ionic liquid by altering GO with a dicationic ionic liquid, 3,3′-(butane-1,4-diyl) bis (1-methyl-1H-imidazol-3-ium) chloride ($[C_4(MIM)_2]Cl_2$). The composite was efficiently explored for its adsorption behavior against chromium ions and the q_m for chromium was noted to be 271.08 mg/g, and even after five cycles q_m remained high above 228.00 mg/g which is impressive and demonstrates the usefulness of ionic liquids based adsorbents for heavy metal removal. Even cellulose has been modified using ionic liquid and efficiently used as adsorbent for removal of p-arsanilic acid [37]. The various materials has been modified using ionic liquids and used as effective adsorbent few of them includes IL-MWCNTs composite tablet for adsorption of antibiotics and metal ions [38]. Mesoporous poly(N,N′-methylene-bis(1-(3-vinylimidazolium)) chloride), was utilized for the anionic dyes (Congo red, Sunset yellow, Acid orange 7, Reactive blue 19) removal [39]. Cellulose microspheres modified with various IL groups were effectively utilized for the removal of acid orange 7 dye [40]. SiO_2 nanoparticles were functionalized with cationic poly(ILs) and were further used for Congo red removal [41]. Chitosan/porous carbon composite (C-PC) modified with 1-Allyl-3-methyl imidazolium bromide [AMIM][Br] and applied for the adsorption of acid blue-25 dye [42]. 1-butyl-3-methylimidazolium chloride modified montmorillonite was used for dye removal [43]. GO-IL composites using 3-n-Hexadecyl-1-vinylimidazolium bromide ($[C_{16}VIm^+]$ $[Br^-]$) as the monomer were employed for the remediation and separation of chromium ions and sunset yellow dye [44]. Porous organic poly(vinylbenzyl chloride-divinylbenzene) copolymer modified with 1-(4-pyridyl)ethan-1-one and 1-(4-pyridyl)undecan-1-one was noted to be extremely effective in exclusion of Zn(II), Cu(II) and Cd(II) ions [45]. Keeping in view above discussed importance of ionic liquid based adsorbents in the present paper, we have studied magnetic IL based nanocomposites [$NiFe_2O_4$@BMSI]Br and explored it as novel adsorbent for Cd(II) ions removal from aqueous medium. The various adsorption parameters, isotherms, kinetics and thermodynamics studies were investigated in detail.

2. Experimental set-up

2.1. Synthesis of [$NiFe_2O_4$@BMSI]Br nanocomposite

As explained in our previous study [46], [$NiFe_2O_4$@BMSI]Br was synthesized by using, $FeCl_3{\cdot}6H_2O$, 1-butylimidazole, $Cd(NO_3)_2{\cdot}4H_2O$, $NiCl_2{\cdot}2H_2O$, (3-bromopropyl) trimethoxysilane, NH_4OH, NaOH, CH_3OH, 1-butylimidazole (98%), H_2SO_4 and $CH_3COOCH_2CH_3$ which were obtained from Sigma-Aldrich. The nanoparticles of $NiFe_2O_4$ were synthesized using the same method as reported earlier [47]. [BMSI]Br was also prepared according to the reported method [48]. After that, 1.6 g [BMSI]Br and 100 mL dry toluene were mixed and then 5.0 g of $NiFe_2O_4$ was added into this well-mixed solution; stirred under Ar for 36 hrs [49]. Finally, the dull-white solid was separated using external magnet and washed 3 times using toluene to remove extra [BMSI]Br. The resulting solid was then dried at 70°C under vacuum and labelled as [$NiFe_2O_4$@BMSI]Br.

2.2. Adsorption capacity evaluation

The adsorption capacity of [$NiFe_2O_4$@BMSI]Br was evaluated by the adsorption of Cd(II) metal ion from aqueous medium. The adsorption experiment of Cd(II) metal ion was performed in a batch system at room temperature. Various parameters were also evaluated, including contact time 1–210 min, temperature 25°C–40°C, pH 2–8 and initial conc. of Cd(II) metal ion 25–100 ppm were also performed to get the optimal values for Cd(II) adsorption onto [$NiFe_2O_4$@BMSI]Br. Adsorption experiments with varying initial concentrations showed that 25 ppm was the appropriate concentration which was kept throughout the experiment. The solution pH during the study was maintained by adding the suitable amount of 0.1 M HCl/NaOH. The thermodynamics, isotherm and kinetics studies were also accomplished by batch method. To find the optimal contact time, 100 mg [$NiFe_2O_4$@BMSI]Br was shaken with 250 mL of 25 ppm Cd(II) metal ion solution at 150 rpm for a fixed time. After a definite time breaks, some sample of the solution was taken out and the conc. of Cd(II) was determined by AAS.

The adsorption capacity of [$NiFe_2O_4$@BMSI]Br was calculated using the following equations [50]:

$$q_e, \text{mg/g} = C_0 - C_e \times \frac{V}{m} \quad (1)$$

where C_0: initial Cd(II) ion concentration in the solution phase; C_e: equilibrium conc. of Cd(II) in the solution phase; q_e: absorption capacity for Cd(II) by [$NiFe_2O_4$@BMSI]Br adsorbent (mg/g); V: volume of Cd(II) solution; m: mass of [$NiFe_2O_4$@BMSI]Br adsorbent.

To study the isotherm model, the adsorption of Cd(II) metal ion using [$NiFe_2O_4$@BMSI]Br nanocomposite was performed at pH 7 with initial conc. ranged from 25 to 80 ppm with 150 mg of adsorbent at the temperature 25°C and 35°C. The thermodynamics studies were also accomplished in the temperature range between 298 and 308 K. The kinetic study for Cd(II) adsorption onto [$NiFe_2O_4$@BMSI]Br nanocomposite (m: 50 mg; C_o: 25, 50, 75 ppm; pH: 7) was performed in the time range 2–120 min. The thermodynamic study for the removal of Cd(II) metal ion using [$NiFe_2O_4$@BMSI]Br nanocomposite was done at 25°C, 30°C and 35°C.

3. Results and discussion

3.1. Optimization of adsorption parameters

The solution's initial pH value is one of the most critical parameters affecting the adsorption process [51]. The effect of pH on the adsorption of Cd(II) metal ion onto [$NiFe_2O_4$@BMSI]Br nanocomposite was studied in the range of 2–8. The pH adjustment of the respective experiments was done with 0.1 M HCl/NaOH solution. Results achieved have been shown in Fig. 1a. It was noted that adsorption of Cd(II) was increased with the increase of solution pH. The maximum adsorption percent was obtained at pH 6 which was 74.3% and it was same at pH 7 also. So, pH 7 was designated as the optimum pH for the succeeding experimental sets. At lower pH (pH < 6), there was strong electrostatic repulsion between [$NiFe_2O_4$@BMSI]Br nanocomposite and Cd(II) metal ion due to the protonation of the material at lower pH and there was a competition adsorption between the Cd(II) metal ion and large amount of H^+ in solution, causing in a lower Cd(II) adsorption percentage [52]. It is significant to see that the adsorption percentage at pH 6 was about 3.4 times of that at pH 2 which may be due to the decrease in the protonation degree of [$NiFe_2O_4$@BMSI]Br as well as the H^+ conc. in solution with increasing the solution pH.

The effect of the contact time on the adsorption of Cd(II) metal ion onto [$NiFe_2O_4$@BMSI]Br is represented in Fig. 1b. It is clear from Fig. 1a that maximum adsorption of Cd(II) ion (74%) was attained in 180 min. The adsorption was only 22% at 15 min and it was reached around two times (42.2%) within 45 min. Actually, in the starting, the adsorption sites of metal ions and the adsorbents were enough for the adsorption process. Henceforth, the adsorption rate was rapid. With the time increasing, the number of available

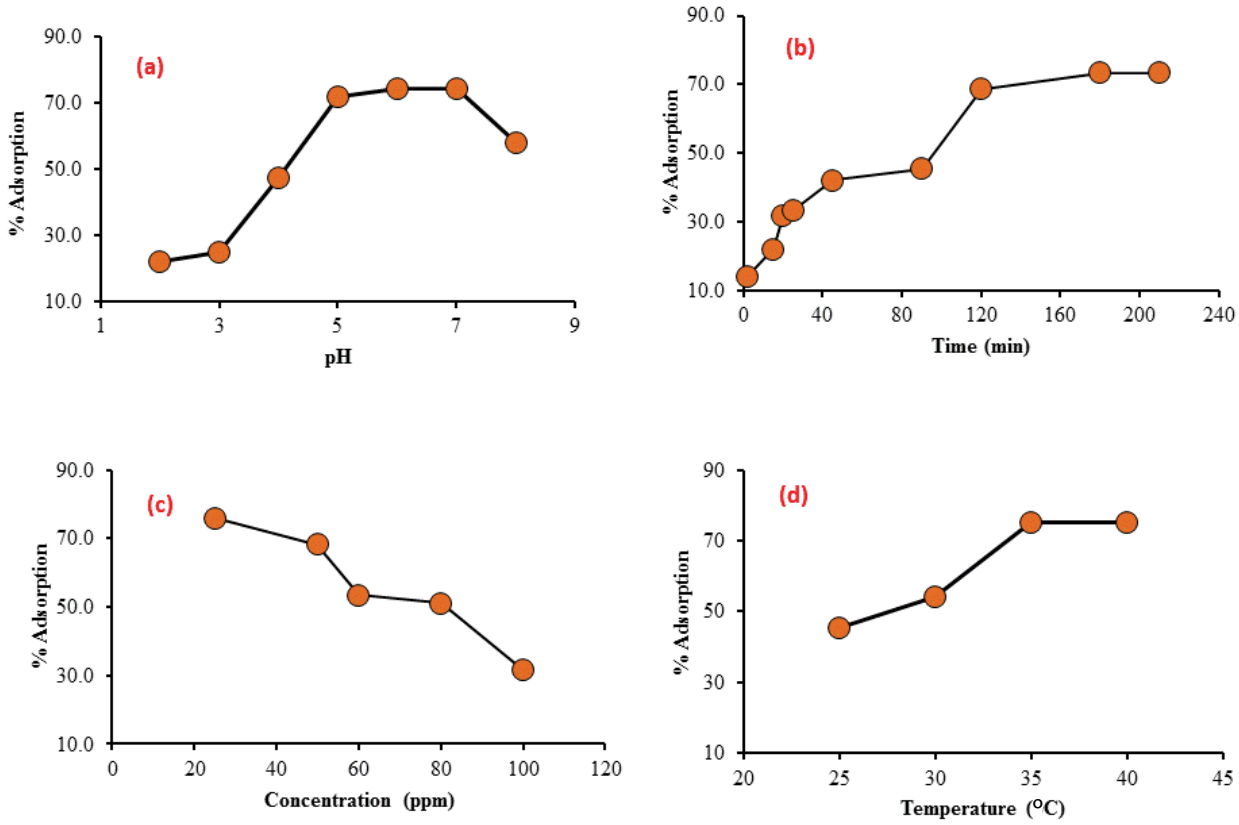

Fig. 1. Effect of pH (a) contact time and (b) initial Cd(II) concentration and temperature on the adsorption of Cd(II) onto [$NiFe_2O_4$@BMSI]Br.

adsorption site and metal ions both reduced, suggesting to the reduction in the adsorption rate [53].

The initial conc. of the adsorbate also plays the important role in the adsorption process. Here, the adsorption of Cd(II) was decreased from 76% to 31.5% (Fig. 1c) with increasing the conc. of Cd(II) solution from 25 to 100 mg/L which might be owing to the fewer accessibility of adsorption sites on the surface of [$NiFe_2O_4$@BMSI]Br adsorbent at higher dose of Cd(II) metal ion [54,55]. Temperature also played a positive role for the adsorption of Cd(II) metal ion using [$NiFe_2O_4$@BMSI]Br. At 25°C the adsorption of Cd(II) metal ion was only 45.3% which was reached up to 75.2% at 35°C and after that no change was observed at 45°C (Fig. 1d). The increase in the adsorption with increasing the temperature suggested the endothermic nature of adsorption [56]. A mechanism for the adsorption of Cd(II) metal ion using [$NiFe_2O_4$@BMSI]Br adsorbent is shown in Fig. 2.

3.2. Adsorption kinetics

Adsorption kinetics is one of the significant features that expresses the efficiency of an adsorbent, which can designate the rate of adsorption of an adsorbent and explore the adsorption mechanism. Pseudo-first-order [57] and pseudo-second-order [58] kinetic models were utilized to interpret the Cd(II)-adsorption data using [$NiFe_2O_4$@BMSI]Br nanocomposite. The formulas for the pseudo-first-order and pseudo-second-order may be used as given below.

Pseudo-first-order model is given as:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1 t}{2.303} \tag{2}$$

Pseudo-second-order model can be demonstrated as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

The fitting parameters of pseudo-first-order and pseudo-second-order models are summarized in Table 1. The value of linear correlation coefficient (R^2) discloses the degree of agreement between the model and the actual situation. By relating the R^2 values of pseudo-first-order and pseudo-second-order kinetics, it was noted that the R^2 values of pseudo-first-order model was better than that of pseudo-second-order, which was nearer to 1, representing that it has a better linear relationship (Fig. 3).

3.3. Adsorption isotherms

The Langmuir [59] and Freundlich [60] isotherm models were selected to fit the data and describe the correlations. The Langmuir isotherm assumes a monolayer adsorption on a homogenous surface where every adsorption sites can only bind one adsorbate and adsorption energy of all adsorption sites is constant. Langmuir isotherm equation may be given as:

$$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{bQ_m C_e} \tag{4}$$

where q_e and C_e are the adsorption capacity and the equilibrium conc. of adsorbate, respectively. Q_m is the maximum adsorption capacity of [$NiFe_2O_4$@BMSI]Br and b is the Langmuir constant.

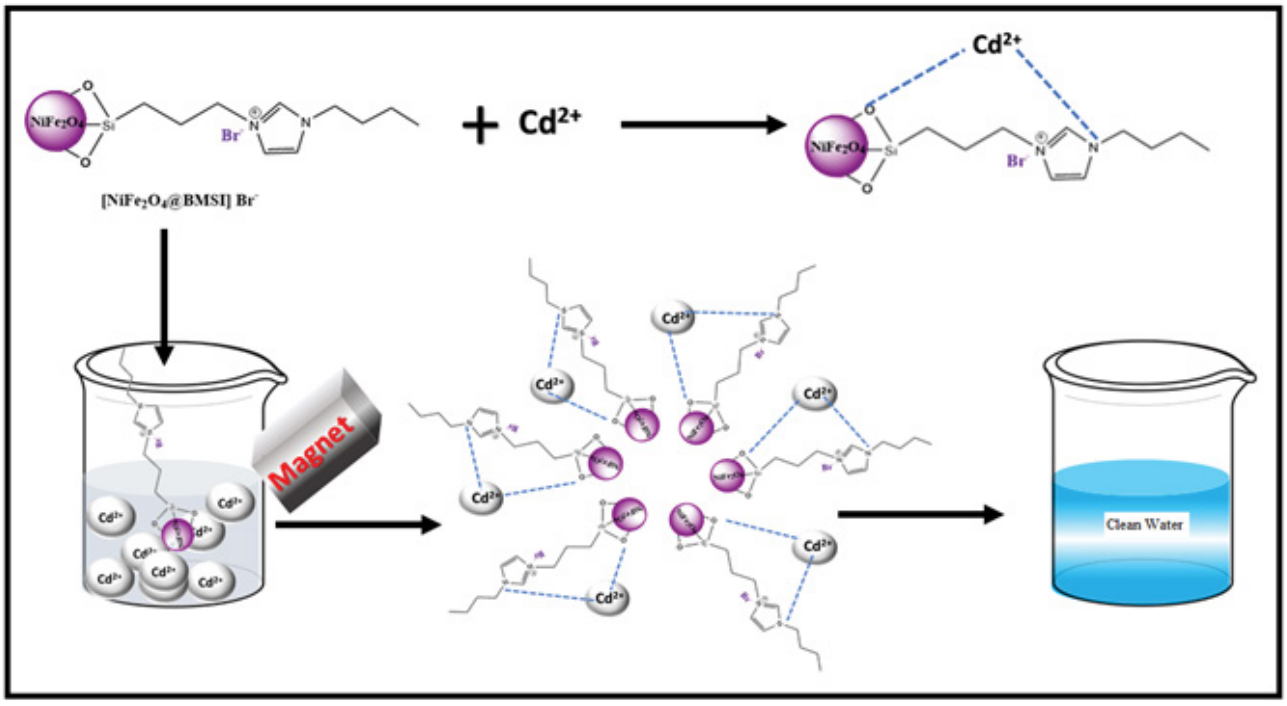

Fig. 2. Mechanism for the interaction Cd(II) metal ion onto [$NiFe_2O_4$@BMSI]Br.

The logarithmic form of Freundlich model is given as:

$$\log q_e = \log K_f + \frac{1}{n}\ln C_e \quad (5)$$

where, n and K_f are the Freundlich adsorption constants related to adsorption intensity and adsorption capacity, respectively.

The values of n represent deviation from linearity of adsorption process.

If $n < 1$ (chemical adsorption process); $n = 1$ (linear adsorption process); $n > 1$ (physical adsorption process).

Fig. 4a and b display that Langmuir model correlated better than Freundlich model with the experimental data for the adsorption of Cd(II) onto [$NiFe_2O_4$@BMSI]Br. This is further confirmed by its higher R^2 values (Table 2).

The value of q_m was 103.09 mg/g which was obtained using Langmuir equation at room temperature and it was slightly increased with the increase in temperature.

Table 1
Kinetic factors for the adsorption of Cd(II) ion onto [$NiFe_2O_4$@BMSI]Br nanocomposite

Kinetic models	Parameters	25 ppm	50 ppm	75 ppm
Pseudo-first-order	q_e (mg/g)	81.75	161.73	22.59
	k_1 (min^{-1})	1.88×10^{-2}	1.79×10^{-2}	1.38×10^{-2}
	R^2	0.992	0.995	0.990
Pseudo-second-order	q_e (mg/g)	101.01	200	270.3
	k_2 (g/mg·min)	3.26×10^{-4}	1.44×10^{-4}	1.26×10^{-4}
	R^2	0.940	0.941	0.958

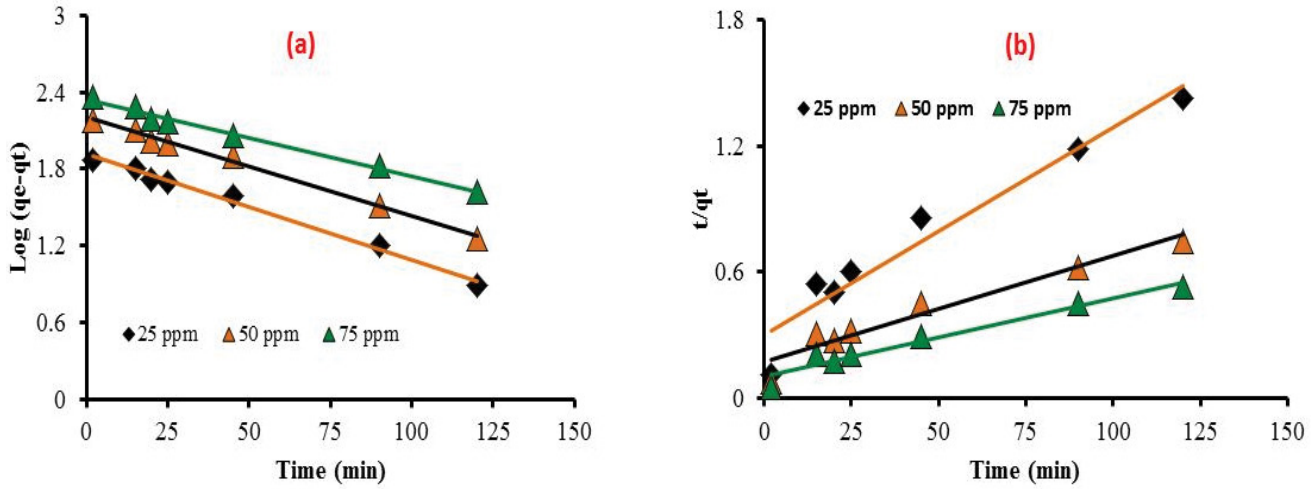

Fig. 3. Adsorption kinetics fitted with pseudo-first-order (a), and pseudo-second-order (b).

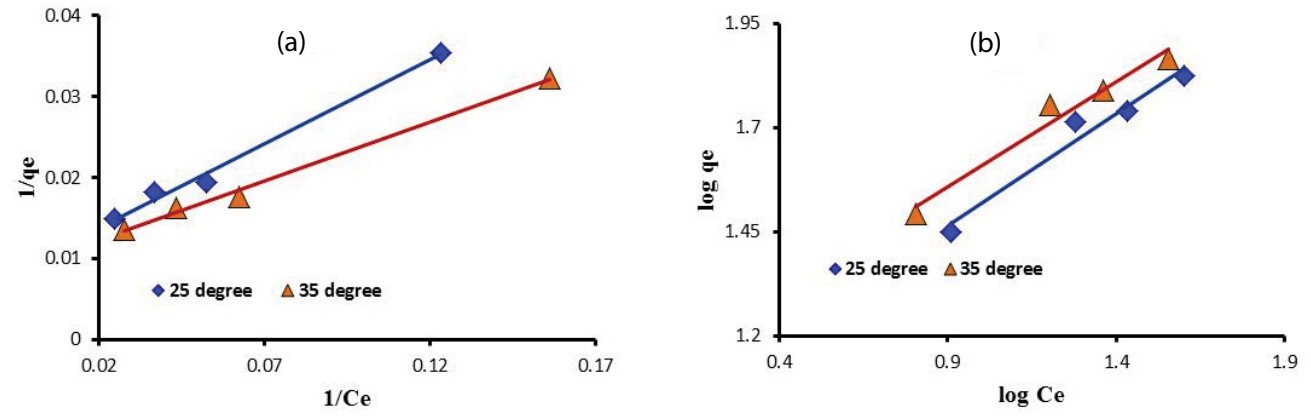

Fig. 4. Langmuir (a) and Freundlich (b) model fits for Cd(II) adsorption onto [$NiFe_2O_4$@BMSI]Br.

Table 2
Isotherm parameters for the adsorption of Cd(II) ion onto [$NiFe_2O_4$@BMSI]Br nanocomposite

Equilibrium model	Parameters	25°C	35°C
Langmuir isotherm	q_m (mg/g)	103.09	106.4
	b (L/mg)	4.68×10^{-2}	6.48×10^{-2}
	R_L	0.46	0.38
	R^2	0.991	0.995
Freundlich isotherm	K_f (L/mg)	9.56	12.8
	n	1.99	1.86
	R^2	0.964	0.966

Table 3
Thermodynamics parameters for the adsorption of Cd(II) onto [$NiFe_2O_4$@BMSI]Br nanocomposite

C_o (mg/L)	$\Delta H°$ (J/mol)	$\Delta S°$ (J/mol·K)	$\Delta G°$ (J/mol)		
			298 K	303 K	308 K
20	50.29	16.97×10^{-2}	–0.28	–1.13	–1.97

A dimensionless constant called the Langmuir separation factor R_L, which is computed as Eq. (7).

$$R_L = \frac{1}{\left(1 + K_L C_0\right)} \tag{6}$$

where c_0 (mg/L) is the initial conc. of Cd(II) and K_L (L/mg) is the constant related to the energy of adsorption (Langmuir Constant). In the present study, R_L was between 0 and 1 which indicated the favourable adsorption of Cd(II) metal ion onto [$NiFe_2O_4$@BMSI]Br.

Moreover, the R_L values decreased with increasing the temperature. It was 0.46 at 25°C and 0.38 at 35°C which showed that the adsorption was more promising at higher temperature. The intensity factor (n) of Freundlich model was more than one which also indicated the promising adsorption of Cd(II) metal ion onto [$NiFe_2O_4$@BMSI]Br.

3.4. Adsorption thermodynamics

In order to achieve insight into the mechanism involved in the adsorption, various thermodynamic parameters for Cd(II) metal ion adsorption using [$NiFe_2O_4$@BMSI]Br, such as $\Delta G°$ (free energy change), $\Delta S°$ (entropy change) and $\Delta H°$ (enthalpy change) were calculated. The values of $\Delta H°$ and $\Delta S°$ were evaluated from the slopes and intercepts of the plots of $\log k_c$ vs. $1/T$ by using the following equations:

$$\log k_c = -\frac{\Delta H°}{2.303RT} + \frac{\Delta S°}{2.303R} \tag{7}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{8}$$

The stated three parameters help in defining the spontaneity, feasibility and exothermic or endothermic nature of the adsorption between adsorbed Cd(II) metal ion and [$NiFe_2O_4$@BMSI]Br nanocomposite. The results of thermodynamic studies are given in Table 3. As can be seen from the values of $\Delta G°$ achieved at all three temperatures (298, 303 and 313 K) were negative (–0.28, –1.13, –1.97), representing that the adsorption of Cd(II) on [$NiFe_2O_4$@BMSI]Br nanocomposite was spontaneous, more favourable at higher temperature and increasing Cd(II)-adsorption capacity with increasing temperature showed that the adsorption process was primarily chemical. The adsorption was endothermic as the value of $\Delta H°$ was positive. The value of $\Delta S°$ was positive which revealed the higher randomness at solid/solution interface throughout the adsorption.

4. Conclusion

Here, the removal of Cd(II) metal ion using [$NiFe_2O_4$@BMSI]Br nanocomposite was studied by batch method. According to the adsorption experimental findings, contact time, pH, temperature and Cd(II) ion concentration affected the adsorption of Cd(II) onto [$NiFe_2O_4$@BMSI]Br nanocomposite. From the study of operating parameters, the optimum pH 7, contact time 180 min and temperature 35 was achieved. The experimental data followed the Langmuir model, thereby suggesting homogeneous monolayer adsorption of Cd(II) on the surfaces of [$NiFe_2O_4$@BMSI]Br nanocomposite. The value of q_m was 103.09 mg/g which was achieved using Langmuir equation at room temperature and it was slightly increased with the increase in temperature. Thermodynamic analysis showed that Cd(II) adsorption was spontaneous and endothermic process.

Acknowledgement

This project was funded by the National Plan for Science, Technology and Innovation (MAARIFAH), King Abdulaziz City for Science and Technology, Kingdom of Saudi Arabia (Award Number 14-ENV591-02).

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