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ON DOUBLE-WALLED CARBON
NANOTUBES/IRON OXIDE COMPOSITE**

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ADSORPTION OF CADMIUM IONS FROM WATER ON DOUBLE-WALLED CARBON NANOTUBES/IRON OXIDE COMPOSITE

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Abstract. A new material (DWCNT/iron oxide) for heavy metals removal was developed by combining the adsorption features of double-walled carbon nanotubes with the magnetic properties of iron oxides. Batch experiments were applied in order to evaluate adsorption capacity of the DWCNT/iron oxide composite for cadmium ions. The influence of operating parameters such as pH value, amount of adsorbent, initial adsorbate concentration and agitation speed was studied. The adsorption capacity of the DWCNT/iron oxide adsorbent for Cd²⁺ ions was 20.8 mg g⁻¹, which is at the state of the art. The obtained results revealed that DWCNT/iron oxide composite is a very promising adsorbent for removal of Cd²⁺ ions from water under natural conditions. The advantage of the magnetic composite is that it can be used as adsorbent for contaminants in water and can be subsequently controlled and removed from the medium by a simple magnetic process.

Keywords: double-walled carbon nanotubes, iron oxide, adsorption, cadmium ions.

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Introduction

Carbon nanotubes (CNTs) have attracted much attention worldwide since their discovery in 1991 [1]. CNTs are relatively new materials that due to their unique electrical, mechanical, optical and chemical properties [1], are used in an increasing number of applications, such as hydrogen storage [2,3] catalyst supports [4], chemical sensors [3,5] nanoelectronic devices [6], and even as tools for daily use, including water purification process [3].

Due to their high specific surface area as well as their layer structure, CNTs seem hold an important place in several fields of application, among those, they have been used as adsorbents for various organic contaminants and metal ions. CNTs can be easily modified by a chemical treatment to increase their adsorption properties [7]. Oxidation of CNTs has been widely reported [8] and different type of metals and oxides have been successfully supported on CNTs such as Ni, Cu, Pt, Fe, Co, SiO₂ [9], SnO₂ [10], Al₂O₃ [6] and TiO₂ [11].

Metal ions are harmful pollutants on ecosystems; their presence in the environment can affect aquatic bodies with serious consequences to biological systems. Water contamination by heavy

metal ions had become much more serious with a rapid development of industries and competitive use of fresh water in many parts of the world. Therefore, heavy metal ions removal from water has become an important issue [11,12,13].

Cadmium, a non-essential and highly toxic metal, is used in the production of alloys, batteries, metal plating, ceramics, dyes and pigments [14,15]. It can be easily routed to drinking water and even at very low concentrations can affect health by causing serious diseases mainly affecting the bones, lungs and kidneys and can even cause some cancers [15,16]. In the field of water treatment, several ways to remove heavy metals from water are known, such as adsorption, coagulation, precipitation, electro dialysis, membrane separation and oxidation processes. However, adsorption process seems to be one of the most effective methods and presents several advantages due to its low-cost and easy usage.

In this work we report the synthesis of a new material (DWCNT/iron oxide) with magnetic properties, composed by double-walled carbon nanotubes and iron oxides. Magnetic nanoparticles of iron oxide are gaining importance as they can be used as highly efficient and

economically viable adsorbents [17]. The capacity of DWCNT/iron oxide for adsorption of Cd^{2+} ions from aqueous solution was evaluated. The influence of contact time, initial adsorbate concentration, pH and adsorbent doses was studied. The obtained results show that the future prospect of this particular adsorbent is very promising for the Cd^{2+} ions removal from industrial effluents.

Experimental

All chemicals were purchased from Sigma Aldrich and used without further purification.

Synthesis of DWCNT/iron oxide composite

The DWCNTs (ca. 80%) were synthesized by catalytic chemical vapour deposition with an outer diameter ranging between 1.2 and 3.2 nm. The resulting material turned out to be individual or gathered in small diameter bundles (10–30 nm), which can be up to ca.100 μm in length [18].

The oxidation of DWCNTs has been performed with nitric acid (50% at 70°C for 12 hrs), according to the method described in the literature by Flahaut *et al.* [18]. After filtration and washing with deionised water, the DWCNT underwent freeze-drying for 24 hrs.

DWCNT/iron oxide composite was prepared by adding variable amounts of oxidized DWCNT to a mixture of solutions of 0.1 M iron(III) chloride hexahydrate and 0.05 M iron(II) chloride tetrahydrate (in a molar ratio of 1:2), up to 10 g L^{-1} . The final pH value of the suspension was adjusted to suitable values (in the range from 2 to 8) by the addition of 0.1 N NaOH or 0.1 N HCl solutions. The mixture was stirred for 2 hrs, thereafter, the solution of 5 M NH_4OH was added dropwise at 70°C to precipitate the iron oxides. At the end of the precipitation process, the suspension was cooled down. The product was separated by centrifugation and then washed with deionised water and ethanol. The resulting composite was dried in the oven at 100°C for 2 hrs.

Characterization methods

Various analytical techniques were applied to characterize the DWCNT/iron oxide composite. Thermogravimetric analysis (TGA) in air (1°/min) was used to estimate the amount of CNTs in the composite (TGA Q500 thermogravimetric analyser). The morphology was studied by transmission electron microscopy (TEM) (JOEL 2100F) with a maximum acceleration of 100 kV and maximum magnification of 500 k. The identification of crystal phases and average size of the iron oxides nanoparticles were

performed by X-ray diffraction (XRD) (Bruker D4 ENDEAVOR). The specific surface area of the DWCNT / iron oxide adsorbent was determined by using the Brunauer-Emmett-Teller (BET) theory (Micromeritics Flow Sorb II 2300; samples were degassed for 1 hrs at 120°C). The point of zero charge of adsorbent (PZC) was determined by potentiometric titration.

Batch mode adsorption experiments

For the optimization of the experimental parameters for the Cd^{2+} ions adsorption process, batch experiments were performed at room temperature. The influence of operating parameters such as pH value, amount of adsorbent, initial adsorbate concentration and agitation speed was studied. All the experiments were performed in Erlenmeyer flasks (250 mL capacity); having each one 50 mL of solution. The required amounts of adsorbent were added to Cd^{2+} ions solutions with the concentration of 20 mg L^{-1} , the pH value of the initial solution of cadmium sulphate was adjusted to the appropriate value in the range of 2-8 by addition of HCl or NaOH solutions. The obtained solutions were stirred at different agitation speed (50- 200 rpm) on a rotary shaker for contact time ranging from 10 to 100 min. After adsorption process the adsorbent was separated *via* vacuum filtration and the residual cadmium ions concentration was determined by atomic absorption spectroscopy (AAS).

The adsorbent capacity was calculated according to Eq.(1):

$$q = [(C_i - C_f) \times V] / m \quad (1)$$

where, q – the adsorption capacity, mg g^{-1} ;

C_i and C_f – the initial and equilibrium concentration of cadmium ions in solution, mg L^{-1}

V – volume of solution, L;

M – mass of adsorbent, g.

Results and discussion

Characterization of adsorbent

The magnetic properties of the DWCNT/iron oxide composite were confirmed by a test with a magnet. TGA analysis in air allows the estimation of the amount of DWCNT to about 8-10 wt.% in the DWCNT/iron oxide composite (Figure 1).

The morphology of the oxidized DWCNT and the composite was analysed by TEM (Figure 2). The recorded TEM images show that morphology of oxidized DWCNT sample (Figure 2(a)) did not exhibit any significant difference in comparison with the starting

DWCNT material. TEM images of the composite depicts an entangled network of oxidized DWCNT with clusters of iron oxides nanoparticles, decorating the surface in a quite homogeneous way and the nanoparticles seem to have a diameter mainly ranging from 10 to 30 nm (Figure 2(b-d)).

The specific surface area of DWCNT/iron oxide composite is only $127 \text{ m}^2 \text{ g}^{-1}$, in comparison with $1000 \text{ m}^2 \text{ g}^{-1}$ [18] for the starting DWCNT material. However, this value is quite relevant considering that the adsorbent only contains about 10 wt.% of DWCNT. The point of zero charge of adsorbent (PZC) was at pH value of 6. An average grain size of 22 nm for the iron

oxide nanoparticles was calculated by using the standard Debye Scherer formula [19].

In the employed reaction conditions, four iron oxides are commonly formed: Fe_3O_4 (magnetite), $\gamma\text{-Fe}_2\text{O}_3$ (maghemite), $\alpha\text{-Fe}_2\text{O}_3$ (hematite) and $\alpha\text{-FeO(OH)}$ (goethite) [19,20]. Figure 3 shows the X-ray diffraction patterns of DWCNT/iron oxide composite. All peaks can be associated with the 4 iron oxides mentioned above (there are many overlaps between these 4 structures). The peaks corresponding to the DWCNT cannot be observed due to their very low intensity ((002) line for DWCNT, and residual Co-Mo). XRD analysis thus indicates that the coating on DWCNT is a mixture of different iron oxides.

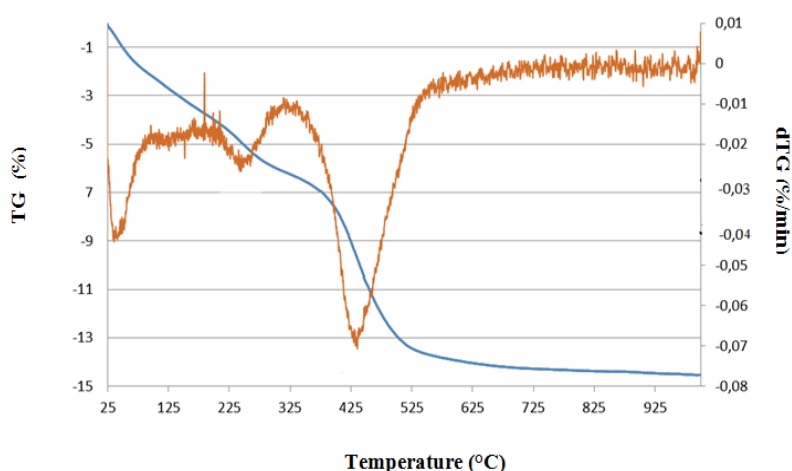


Figure 1. TGA analysis of the DWCNT/iron oxide composite.

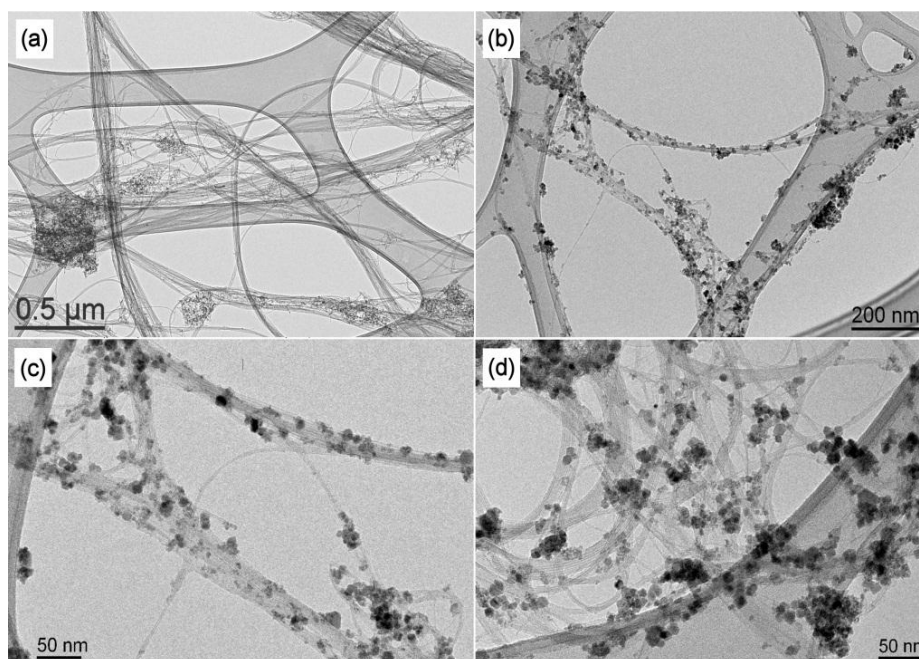


Figure 2. TEM images of (a) oxidized DWCNT and (b), (c), (d) DWCNT/iron oxide composite.

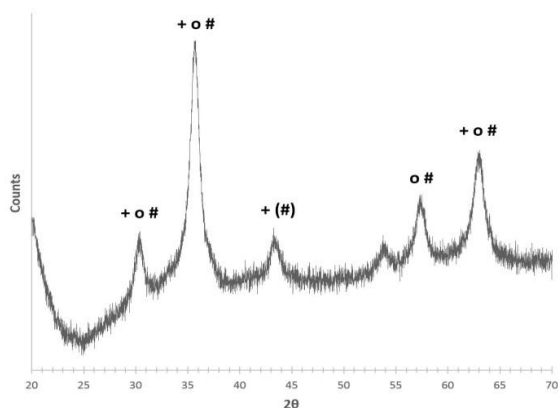


Figure 3. XRD pattern of the DWCNT/iron oxide composite. +: magnetite [01-079-0416]; o: goethite [01-074-3080]; #: maghemite [01-089-5894]. The peak at 54° may correspond to hematite.

Effect of the adsorbent amount

Different amounts, ranging from 10 to 100 mg, of adsorbent were used in batch experiments. The contact time, pH value, concentration of the solution and the agitation speed were fixed respectively at: 2 hrs, 7, 20 mg L⁻¹ and 150 rpm. It can be observed that the percentage of cadmium ions removal increased while increasing the adsorbent amount up to 50 mg and then remained nearly constant over the rest of the range (Figure 4). This result indicates the saturation of adsorption sites on the adsorbent. The maximum adsorption capacity of DWCNT/iron oxide composite for Cd²⁺ ions under the studied conditions is 19.73 mg g⁻¹.

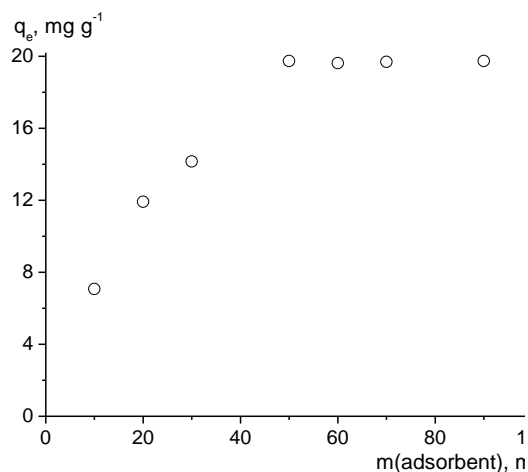


Figure 4. The effect of adsorbent amount on the adsorption capacity for cadmium ions. [Cd²⁺] of 20 mg L⁻¹, pH value 7, contact time 2 hrs and agitation speed of 150 rpm.

Effect of contact time

The effect of contact time on adsorption capacity of DWCNT/iron oxide adsorbent for cadmium ions was investigated at pH value of 7, cadmium ions concentration of 20 mg L⁻¹, adsorbent dosage of 50 mg and equilibrium time ranging from 10 min to 24 hrs. The equilibrium of the adsorption process of cadmium ions on DWCNT/iron oxide adsorbent was achieved at 50 min, which corresponds to an adsorption capacity of 19.79 mg g⁻¹ (Figure 5).

Effect of agitation speed

The agitation speed effect on the adsorption capacity of DWCNT/iron oxide adsorbent for cadmium ions was studied in the range from 0 to 200 rpm. The adsorption capacity of DWCNT/iron oxide for cadmium ions increased with increasing agitation speed up to 150 rpm and then it remained constant (Figure 6). At the agitation speed of 150 rpm the thickness of the boundary layer surrounding the adsorbent increases and thus the particles of the mixture are promoted.

Effect of pH on the adsorption process

The pH is an important parameters, it has a great influence on the adsorption processes, such as the removal of heavy metals and determines the applicability of adsorption system in real life condition [15]. In the deionised water are present different forms of cadmium species are presented Cd²⁺, Cd(OH)_{2(s)} and Cd(OH)⁺.

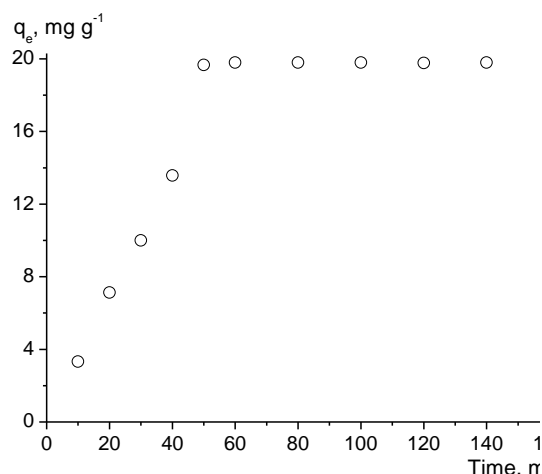


Figure 5. The effect of contact time of cadmium ions adsorption on DWCNT/iron oxide adsorbent. [Cd²⁺] of 20 mg L⁻¹, pH value 7, 50 mg of adsorbent and agitation speed of 150 rpm.

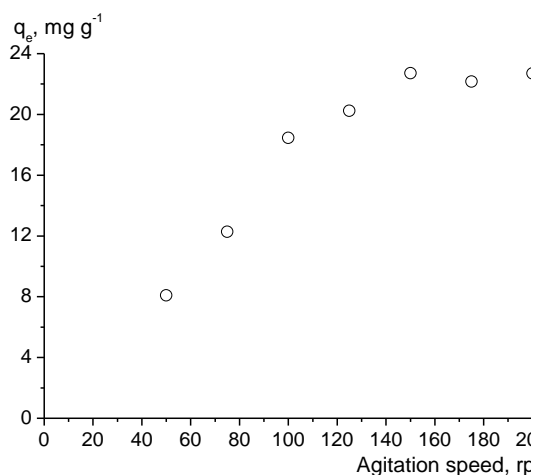


Figure 6. The effect of agitation speed on adsorption of cadmium ions on DWCNT/iron oxide adsorbent. $[Cd^{2+}]$ of 20 mg L⁻¹, pH value 7 and 50 mg of adsorbent.

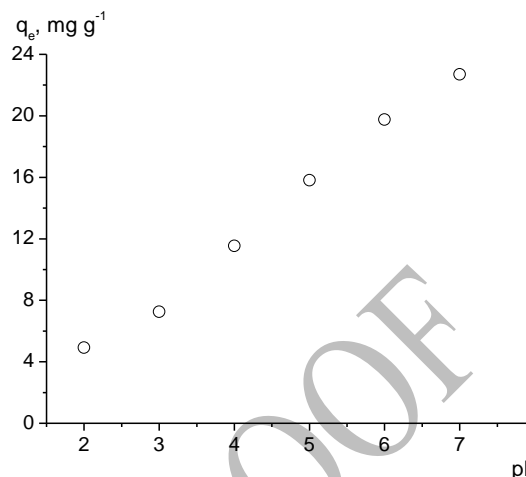


Figure 7. The effect of pH value on adsorption of cadmium ions on DWCNT/iron oxide adsorbent. $[Cd^{2+}]$ of 20 mg L⁻¹, 50 mg of adsorbent and agitation speed of 150 rpm.

However, Cd^{2+} is the dominant cadmium specie at low pH values. It is known that cadmium ions in the solution precipitate above pH of about 8.5. From earlier studies, the ideal pH value for adsorption of cadmium ions from solutions on different adsorbents was within the range of 6 to 8 [15]. Under experimental conditions described in this study, we can expect the precipitation of Cd^{2+} ions above pH 8.2 (the solubility constant of the equilibrium between Cd^{2+} and $Cd(OH)_2$ forms is $5.9 \cdot 10^{-15}$ and the concentration of Cd^{2+} ions in solution is 20 mg L⁻¹).

The effect of pH value on the adsorption of cadmium ions on DWCNT/iron oxide adsorbent is presented in Figure 7. The adsorption value of Cd^{2+} on DWCNT/iron oxide adsorbent increased sharply from 4.92 mg g⁻¹ (at pH 2) to 19.80 mg g⁻¹ (at pH 8), the highest adsorption was obtained at pH 7. According to literature data, in the most of cases, adsorption of Cd^{2+} ions was greater in the alkaline range [21]. By increasing the pH value is induced an increase in the negative charge on the adsorbent surface, which enhance the adsorption capacity due to electrostatic interactions. The higher uptake of Cd^{2+} ions on DWCNT/iron oxide adsorbent at pH 7 was possibly due to ionization of the acidic functional groups into negatively charged carboxylates (pH_{PZC} value of DWCNT/iron oxide adsorbent is 6).

Comparison of adsorbent performance with literature data

Figure 8 shows that only 100 minutes were needed for the complete removal of Cd^{2+} ions from solution. The maximum adsorption capacity of the DWCNT/iron oxide is about 20 mg g⁻¹ while it is only about 14 mg g⁻¹ in the case of the starting DWCNT material (Figure 9). A comparison of q_{max} values for Cd^{2+} adsorption on DWCNT/iron oxide with those reported previously, using different adsorbents, is shown in Table 1. A direct comparison between the studied DWCNT/iron oxide and other adsorbents found in literature was difficult because of the different experimental conditions (initial Cd^{2+} concentration, chemical composition of the adsorbent, pH, temperature, time, etc).

However, it may be seen that the q_{max} value differs widely for different adsorbents (Table 1). In our experimental conditions, the DWCNT/iron oxide material shows a higher efficiency than other adsorbents. The only adsorbent with a similar activity was ethylenediamine-functionalized MWCNTs [22] but our composite has a strong advantage when it comes to its separation at the end of the process, because the use of a simple magnet could facilitate this operation quite a lot.

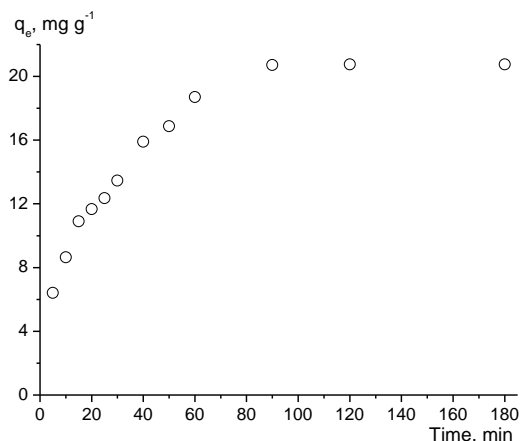


Figure 8. Adsorption capacity of DWCNT/iron oxide for Cd²⁺ ions, at solid/liquid ratio (mg/mL) = 1, [Cd²⁺] of 20 mg L⁻¹, pH of 7, and agitation speed of 150 rpm.

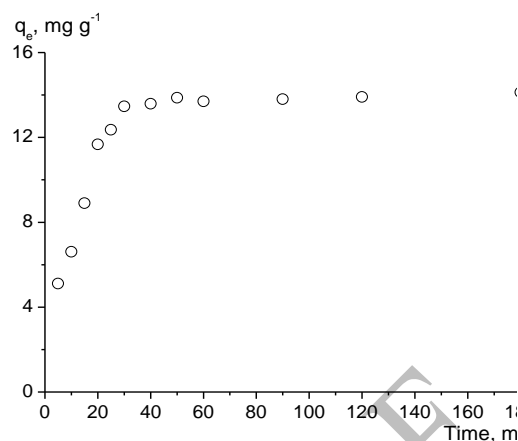


Figure 9. Adsorption capacity of DWCNT for Cd²⁺ ions, at solid/liquid ratio (mg/mL) = 1, [Cd²⁺] of 20 mg L⁻¹, pH of 7, and agitation speed of 150 rpm.

Table 1

Adsorption capacities of different adsorbents for Cd²⁺ ions.

Adsorbent	$q_{max}(mg\ g^{-1})$	Conditions	References
CNT (HNO ₃)	2.92	pH 4.50 and adsorbent 0.15 g	[21]
Acid modified CNTs	2.02	pH 7, adsorbent 50 mg	[23]
Raw CNTs	1.661	pH 7, 1 mg L ⁻¹ and adsorbent 50 mg	[24]
CNT (KMnO ₄)	11	pH 5.5 and 4 mg L ⁻¹	[25]
MWCNT (HNO ₃)	10.86	pH 5, 10 mg L ⁻¹ and room temperature	[26]
Ethylenediamine-functionalized MWCNTs	21.23	5 mg L ⁻¹ and temperature 45 °C	[22]
Oxidized nitrogen-doped MWCNTs	10.5	pH 6, time 40 min, shaking rate 200 rpm and temperature 25 °C	[27]
CNTs (H ₂ O ₂)	2.6	pH 5.5 and 4 mg L ⁻¹	[24]
Hematite	0.24	1 mmol L ⁻¹ , 40 g L ⁻¹ time 2.0 h, temperature 20°C and pH 9.2	[28]
Fe ₃ O ₄ CdTe	8.02	5–100 mg L ⁻¹ , adsorbent 1.670 g L ⁻¹ time: 30 min temperature 30 °C and pH 5.8	[29]
Iron oxide activated red	13.15	adsorbent 6 g L ⁻¹ , time 90 min, temperature 20, pH 6.0 and 100–500 μ g L ⁻¹	[15]
Amino-functionalized silica	18.28	5 g L ⁻¹ , adsorbent 50 mg and pH 5	[30]
Manganoxide mineral	6.8	adsorbent 50 mg L ⁻¹ , 300 rpm, 1 g and temperature 25 °C	[31]
Iron oxide coated sewage sludge	14.7	pH 7 and time 60 min	[32]
Sludge of Miyamachi DWTP	5.3	pH 6 and time 120 min	[33]
Sludge of Nishino DWTP	9.2	pH 6 and time 120 min	[33]
Na-zeolitic tuff	18	5 mg/L, pH 6.5 and time 60 h	[34]
Carbonaceous material	15	5 mg/L, pH 6.5 and time 60 h	[34]
DWCNT /iron oxide	20.76	150 rpm, 20 mg L ⁻¹ and adsorbent 50 mg	This study

Conclusions

A new DWCNT/iron oxide magnetic composite was prepared and characterized by XRD, TGA, and TEM methods. XRD data suggest that the magnetic phase is mainly composed of maghemite and magnetite.

For the optimization of the experimental parameters of adsorption of Cd²⁺ ions on DWCNT/iron oxide adsorbent, batch experiments were performed. At optimum experimental conditions, (cadmium ions concentration of 20 mg L⁻¹, pH value of 7, solid/liquid ratio (mg/mL) = 1, contact time of 50 min and agitation speed of 150 rpm) the removal efficiency higher

than 95% was achieved. Obtained results reveal that the adsorbent material efficiency depends on the solution pH, and as listed in the literature pH 6–8 is favourable for adsorption of cadmium ions. Under experimental conditions, the adsorption capacity of DWCNT/iron oxide for cadmium ions is about 20 mg g⁻¹, which is at the state of the art.

The synthesized DWCNT/iron oxide composite turned out to be a suitable and promising material in the water treatment field, based on several advantages in terms of processing efficiency, where heavy metals can be separated *via* magnetic forces, representing thus an important innovation in this field.

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