EVALUATION OF TEA WASTES EFFICIENCY ON REMOVAL OF COPPER (II) AND NICKEL (II) IONES FROM AQUEOUS SOLUTIONS

[1]MEHRDAD CHERAGHI, [2]SOHEIL SOBHANARDAKANI, [3]BAHAREH LORESTANI, [4]RAZIYEH ZANDIPAK

[1,2,3]Department of the Environment, College of Basic Sciences, Hamedan Branch, Islamic Azad University, Hamedan, Iran,
[4]Young Researchers & Elite Club, Hamedan Branch, Islamic Azad University, Hamedan, Iran
Email: [1]cheraghi.mehrdadd@gmail.com, [2]s_sobhan@iauh.ac.ir, [3]saba12ir@yahoo.com, [4]raziyeh.zandi@yahoo.com

Abstract- A batch system was applied to study the adsorption of Cu(II) and Ni(II) from aqueous solution using tea wastes. The effects of solution pH, tea wastes dose, initial metals concentration and contact time on the adsorption were investigated. The experimental data were analyzed using the Langmuir and Freundlich models of adsorption. Equilibrium data fitted well with the Langmuir model with maximum adsorption capacity of 125 and 111 mg g^{-1} for Cu(II) and Ni(II), respectively.

Keywords- Adsorption, Tea Wastes, Copper, Nickel, Removal Efficiency.

I. INTRODUCTION

Heavy metals are classified among the most dangerous groups of anthropogenic environmental pollutants due to their toxicity and persistence in the environment (1-3). Heavy metals such as copper and nickel are non-degradable and they can accumulate in the food chain (4,5). The main source of nickel pollution in the water derives from industrial production processes such as galvanization, smelting, mining, batteries manufacturing and metal finishing (6). Exposure to nickel may cause cancer of lungs, nose and bones. Moreover, it may cause extreme weakness, dermatitis, headache, dizziness and respiratory distress (7). Copper is one of the toxic heavy metals found in various industrial waste waters like dyeing, paper, and petroleum and can cause health problems such as hemolysis, liver and kidney damage, irritation of upper respiratory tract, gastrointestinal disturbance and diarrhea (8). Many treatment processes, such as oxidation, reduction, precipitation, membrane filtration, ion exchange and adsorption have been used to remove metal ions from aqueous solutions (9,10). Among waste waters treatment technologies, adsorption is cheap and effective (11). Activated carbon is the most commonly used adsorbent for metals removal from waste water. However, its widespread application is restricted due to high cost and difficult disposal (12,13). Most of the recent research activities evaluate the properties of various low-cost adsorbents that have potential applications. Agriculture wastes or by-products have been investigated extensively for the removal of heavy metals due to their abundance in nature (14,15). Numerous waste biomass sources are available in different parts of the world, on which some experimental adsorption properties have been reported, for example, rice husk, peanut shells, corn cobs, saw dust, coir dust, dry tree leaves and barks, tea and coffee waste, rice and wheat bran, and sea weeds (16,17). Some studies have demonstrated the ability of tea wastes to remove synthetic dyes, turbidity and even some types of heavy metal ions from water (18-21).

In this study, tea wastes were employed in batch process for removal of Cu(II) and Ni(II) from aqueous solution. The effect of pH, initial concentration, contact time, and tea wastes dose were investigated. Isotherm of adsorption was evaluated.

II. DETAILS EXPERIMENTAL

2.1. Apparatus

All Cu(II) and Ni(II) concentrations were measured using a inductively coupled plasma spectrometry (Verian710-Es Australia). All pH measurements were made with a 780 pH-meter (Metrohm Switzerland) with a combined glace-calomel electrode.

2.2. Reagents

$Cu(NO_3)_2 \cdot 3H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, hydrochloric acid and sodium hydroxide with the highest purity available were purchased from Merck (Darmstadt, Germany). Double-distilled water was used in all experiments. Stock solution of Cu(II) and Ni(II) were prepared by dissolving $Cu(NO_3)_2 \cdot 3H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ in double-distilled water. The solutions of different initial concentrations were prepared by diluting the stock solution in appropriate proportions.

2.3. Preparation of the tea wastes

Tea wastes were prepared from black teas available in Iranian market. This tea waste has been washed at the first step and then rinsed with double-distilled water. After drying at 85°C, it was ground and screened (using screen with mesh size 10). In order to preserve, it was kept in plastic stopper bottle

(containers), and to minimize in contact with humidity, all these bottles were preserved in desiccators before the time of use (17). Chemical and physical properties of the adsorbents are presented in Table 1.

Table 1: Physical and chemical properties of tea wastes

Factor	amount	Unit
Humid	10.5	%
Density	0.353	g cm^{-3}
Dissolved material	81	%
Solution particles total	108	mg l^{-1}
Organic matters	85	%
Ash	2.85	%
pH_{ZPC}	5.0	

2.4. Batch adsorption experiments

Adsorption studies were performed by adding 0.25 g of tea wastes to 13 mL of Cu(II) and Ni(II) solutions (1–300 mg L^{-1}) in 100 mL beakers. The pH of the solution was adjusted at 5.0 with 0.1 mol L^{-1} HCl or/and 0.1 mol L^{-1} NaOH solutions and then the mixture was agitated using a magnetic stirrer with the stirring speed 160 $r.min^{-1}$ at room temperature for 75 min. Subsequently, the tea wastes with adsorbed Cu(II) and Ni(II) were separated from the mixture using Whatman filter paper with a diameter of 42µm. The concentration of the Cu(II) and Ni(II) ions which remained in the solution were determined by inductively coupled plasma spectrometry (Verian710-Es Australia) and the concentration of the Cu(II) and Ni(II) ions remained in the adsorbent phase (q_e, mg g^{-1}) were calculated using the Eq. (1);

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e are the initial and equilibrium Cu(II) and Ni(II) concentrations in solution, respectively (mg L^{-1}), V (L) is the volume of solution and W (g) is the weight of adsorbent. Finally, the Cu(II) and Ni(II) removal percent (R%) was calculated by the Eq. (2);

$$R\,(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

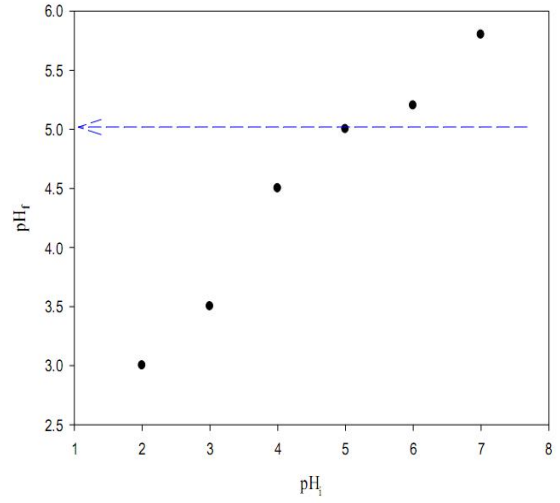


Fig. 1. The determination of the point of zero charge of the tea waste

where C_0 and C_e (mg L^{-1}) were the initial and final Cu(II) and Ni(II) concentrations (22).

RESULTS AND DISCUSSION

3.1. Effect of pH

The pH value of the solution was an important controlling parameter in the adsorption process. The influence of initial pH on the adsorption of Cu(II) and Ni(II) were studied in the range of 2.0-7.0 for initial metals concentration of 30 mg L^{-1} at temperatures 25±1 °C. As shown in Figure 2, the removal efficiencies of Cu(II) and Ni(II) on tea wastes increased significantly with increasing pH from 1.0 to 5.0. The effect of solution pH on adsorption could be explained by the surface charge of the tea wastes. The zero point charge (pH_{ZPC}) for the tea wastes was determined around 5.0 (Figure 1). At lower pH (<pH_{zpc}), the tea wastes surface will be positively charged, creating electrostatic repulsion between the positively charged surface of the tea wastes and Cu(II) and Ni(II) ions. At higher pH (>pH_{zpc}), the number of positively charged sites are reduced and raised the number of negatively charged sites, which increases the electrostatic attractions between Cu(II) and Ni(II) ions and tea wastes surface. The increase in the adsorption of Cu(II) and Ni(II) on tea wastes with increase in the solution pH can be explained based on competition between H^+ ions and M(II) ions for the active surface sites in acidic solutions and also formation of metal ions species such as $CuOH^+$, $Cu(OH)_2$, $NiOH^+$ and $Ni(OH)_2$ of low solubility may contribute in part to maximum percentage removal of metal ions. Similar results were observed by Wang et al. who investigated the effect of pH on removal of Cu(II) from aqueous solution by nanoscale magnetite and indicated that adsorption efficiency increases with increasing pH (8).

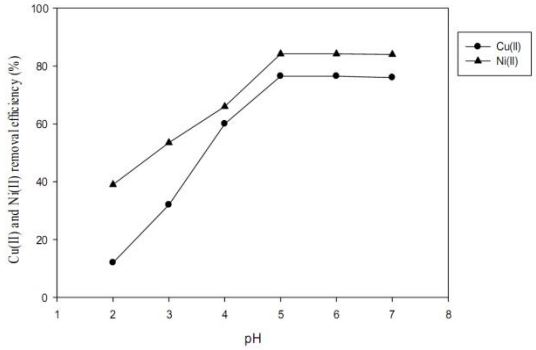


Fig. 2. Effect of pH on the removal of Cu(II) and Ni(II) ions from aqueous solution by tea wastes

3.2. Effect of adsorbent dose

The effect of adsorbent dose on the removal of the Cu(II) and Ni(II) ions was carried out by varying the adsorbent amount from 0.1 to 1.0 g at fixed pH, concentration, and temperatures (25±1 °C). Figure 3, shows that the removal efficiency (%) increased from 43 to 87% for Cu(II) and from 50 to 92% for Ni(II)

with the increase in dose of the tea waste till 0.25 g. Hence, the adsorption studies were performed by selecting 0.25 g of adsorbent. Similar results were reported by Xin et al. in the removal of heavy metals (23).

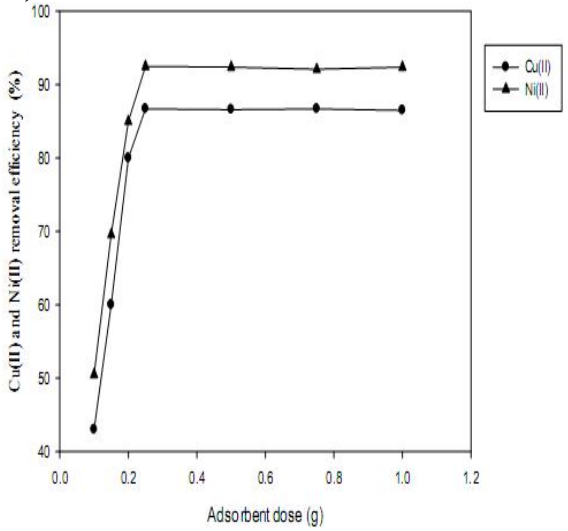


Fig. 3. Effect of adsorbent dose on the removal of Cu(II) and Ni(II) ions from aqueous solution by tea wastes

3.3. Effect of contact time

The contact time was evaluated at initial metals concentration of 30 mg L^{-1} and at pH 5.0. The influence of contact time on the adsorption capacity of tea wastes is shown in Figure 4. It was found that the removal of Cu(II) and Ni(II) ions increases with the increase in the contact time and reaches equilibrium after 75 min. The rapid adsorption in the 60 min first was due to abundant available active sites on the adsorbent. Then, the adsorption rate slows down with the gradual decrease in active sites. Similar phenomena have been observed in the adsorption of Ni(II) by multiwall carbon nanotube/iron oxide magnetic composites (24).

3.4. Effect of initial Cu(II) and Ni(II) concentrations

The effect of initial metals concentration on the adsorption efficiency of Cu(II) and Ni(II) ions was investigated in the initial concentration range of 30–300 mg L^{-1} and at pH 5.0 and temperatures (25±1 °C). The results are shown in Figure 5. It was observed that by increasing the initial metals concentration from 30 to 300 mg L^{-1}, the removal efficiency (%) decreased from 91 to 77% for Cu(II) and from 99 to 80% for Ni(II), although the actual amount of metals adsorbed per unit mass of tea wastes increased. This increase is due to the decrease in resistance to the uptake of solute from metals solution. The initial metals concentration provides an important driving force to overcome the mass transfer resistance of the metal between the aqueous phases and solid phases. Similar findings were reported by Karami, while studying the effect of Cu(II), Zn(II), Pb(II) and Ni(II) adsorption on magnetite nanorods (25).

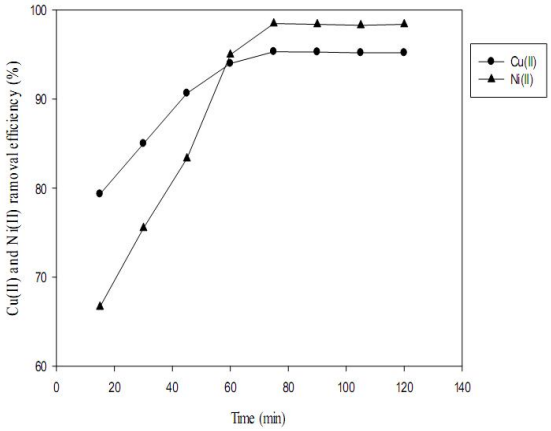


Fig. 4. Effect of contact time on the removal of Cu(II) and Ni(II) ions from aqueous solution by tea wastes

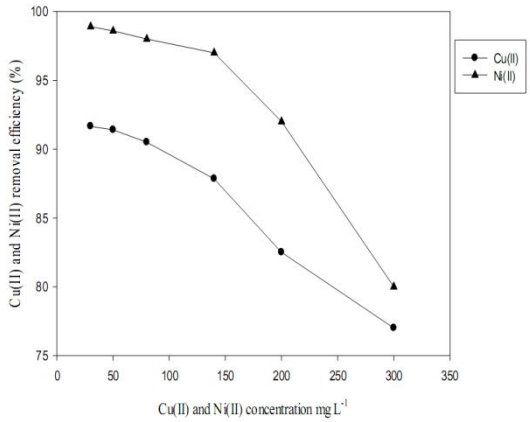


Fig. 5. Effect of initial concentrations on the removal of Cu(II) and Ni(II) ions from aqueous solution by tea wastes

3.5. Equilibrium adsorption isotherm

Isotherms are the equilibrium relations between the concentration of adsorbate on the solid phase and its concentration in the liquid phase. The adsorption equilibrium data of Cu(II) and Ni(II) onto tea wastes were analyzed in terms of Langmuir (Eq. (3)) and Freundlich (Eq. (4)) models. The linear equations are as follows (26);

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b_l} \quad (3)$$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln k_f \quad (4)$$

where c_e (mg L^{-1}) is the equilibrium concentration of Cu(II) and Ni(II) ions in solution, q_e (mg g^{-1}) is the equilibrium adsorption capacity of tea wastes, q_m (mg g^{-1}) is the maximum adsorption capacity of tea wastes for monolayer coverage, b (L mg^{-1}) is a constant related to the adsorption free energy, K_f ($mg^{1-(1/n)}$ $L^{1/n}$ g^{-1}) is a constant related to adsorption capacity, and n is an empirical parameter related to adsorption. Figure 6 shows the adsorption isotherm of Cu(II) and Ni(II) at 25±1 °C using the tea wastes. The Langmuir and Freundlich isotherm parameters for the adsorption of Cu(II) and Ni(II) onto tea wastes are given in Table 2. The correlation coefficient for the Langmuir isotherm is higher in comparison than the value obtained for the Freundlich isotherm, which indicated the homogeneous distribution of active sites

on the surface of tea wastes. Moreover the Langmuir isotherm model assumes the monolayer adsorption of Cu(II) and Ni(II) ions onto adsorbent surface. The results shows that the maximum adsorption capacity (q_m) of tea wastes for adsorption of Cu(II) and Ni(II) were 125 and 111mg g^{-1}, respectively.

Table 2: Isotherm parameters of adsorption of Cu(II) and Ni(II) onto tea wastes

	Langmu			Freundli		
Met	b	q_m (mg g	R^2	K_f (mg^{1-}	n	R^2
Cu	0.0	125	0.99	91.8	1.5	0.97
Ni	0.2	111	0.99	200	2.5	0.94

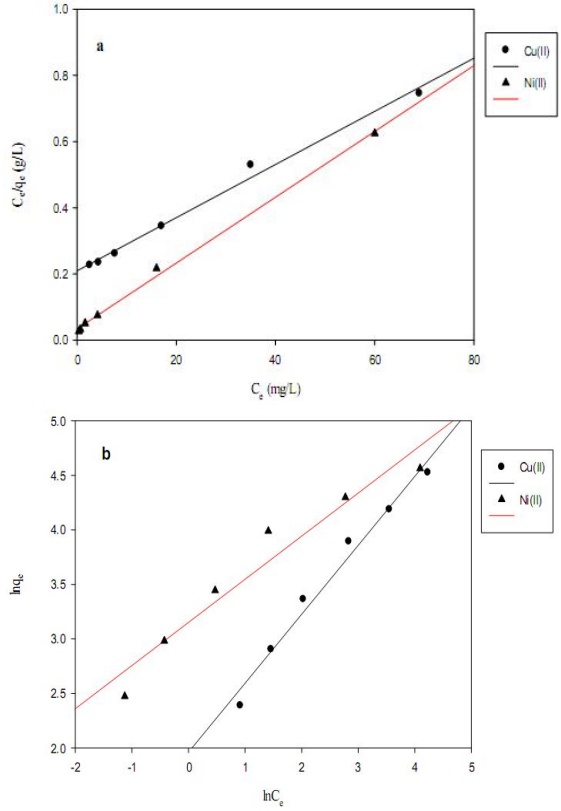


Fig. 8. (a) Langmuir and (b) Freundlich isotherms for Cu(II) and Ni(II) adsorption onto tea wastes at 25±1 ˚C

CONCLUSIONS

The present study shows that the tea wastes are an effective adsorbent for removal of Cu(II) and Ni(II) from aqueous solution. It was observed that the adsorption of Cu(II) and Ni(II) by tea wastes is favored at high pH. The optimum pH for the maximum removal of Cu(II) and Ni(II) was found at pH 5.0. The equilibrium adsorption is achieved in 75 min for Cu(II) and Ni(II). The amount of Cu(II) and Ni(II) adsorption increased with the increase of adsorbent dose. The Cu(II) and Ni(II) equilibrium data were described well with Langmuir isotherms. These results confirm that the tea wastes can be considered as an alternative adsorbent for the removal of metals from industrial waste water.

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REFRENCES

[1]. Y. Zhu, J. Hu, and J. Wang, "Competitive adsorption of Pb(II), Cu(II) and Zn(II) onto xanthate-modified magnetic chitosan", Journal of Hazardous Materials,vol. 221-222,pp.155-161,2012.

[2]. Q. Fei, and W. Bei, "Single and Multi-component Adsorption of Pb, Cu, and Cd on Peat", Bulletin of Environmental Contamination and Toxicology,vol.78,pp. 265-269,2007.

[3]. Y. Li, J. Ding, Z. Luan, Z. Di, Y. Zhu, C. Xu, D. Wu, and B. Wei, "Competitive adsorption of Pb, Cu and Cd ions from aqueous solutions by multiwalled carbon nanotubes", Carbon,vol.41,pp.2787-2792,2003.

[4]. B. Dai, M. Cao, G. Fang, B. Liu, X. Dong, M. Pan, and S. Wang, "Schiff base-chitosan grafted multiwalled carbon nanotubes as a novel solid-phase extraction adsorbent for determination of heavy metal by ICP-MS", Journal of Hazardous Materials,vol.219-220,pp.103-110, 2012.

[5]. H. Wang, A. Zhou, F. Peng, H. Yu, and J. Yang, "Mechanism study on adsorption of acidified multiwalled carbon nanotubes to Pb(II)", Journal of Colloid and Interface Science,vol.316,pp.277-283,2007.

[6]. S. Yang, J. Li, D. Shao, J. Hu, and X. Wang, "Adsorption of Ni(II) on oxidized multi-walled carbon nanotubes: Effect of contact time, pH, foreign ions and PAA", Journal of Hazardous Materials,vol.166,pp.109-116, 2009.

[7]. J.R. Ruparelia, S.P. Duttagupt, Chatterjee, A.K. and S. Mukherji, "Potential of carbon nanomaterials for removal of heavy metals from water", Desalination,vol.232,pp.145-156,2008.

[8]. X.S. Wang, Z. Lei, and J.L. Hai, "Surface chemical properties and adsorption of Cu(II) on nanoscale magnetite in aqueous solutions", Desalination,vol.276,pp.154-160, 2011.

[9]. H. Wang, X. Yuan, Y. Wu, H. Huang, G. Zeng, Y. Liu, X. Wang, N. Lin, and Y. Qi, "Adsorption characteristics and behaviors of graphene oxide for Zn(II) removal from aqueous solution", Applied Surface Science, vol.279,pp.432-440,2013.

[10]. D. Xu, X. Tan, C. Chen, and X. Wang, "Removal of Pb(II) from aqueous solution by oxidized multiwalled carbon nanotubes", Journal of Hazardous Materials,vol.154, pp.407-416,2008.

[11]. H.K. Boparai, M. Joseph, and D.M. O'Carroll, "Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zero valent iron particles", Journal of Hazardous Materials,vol.186,pp.458-465,2011.

[12]. T. Sheela, Y. Arthoba Nayaka, R. Viswanatha, S. Basavanna, and T.G. Venkatesha, "Kinetics and thermodynamics studies on the adsorption of Zn (II), Cd (II) and Hg(II) from aqueous solution using zinc oxide nanoparticles", Powder Technology,vol.217,pp.163-170, 2012.

[13]. S. Azizian, M. Haerifar, and H. Bashiri, "Adsorption of methyl violet onto granular activated carbon: Equilibrium, kinetics and modeling", Chemical Engineering Journal,vol.146,pp.36-41,2009.

[14]. G. Mahajan, and D. Sud, "Application of ligno-cellulosic waste material for heavy metal ions removal from aqueous solution", Journal of Environmental Chemical Engineering,vol.1,pp.1020-1027,2013.

[15]. S.E. Bailey, T.J. Olin, R.M. Bricka, and D.D. Adrian, "A review of potentially low cost sorbents for heavy metals", Water Research,vol.33,pp.2469-2479,1999.

[16]. S. Sobhanardakani, H. Parvizimosaed, and E. Olyaie, "Heavy metals removal from waste waters using organic solid waste—rice husk", Environmental Science and Pollution Research,vol.20,pp.5265-5271,2013.

[17]. B.M.W.P.K. Arasinghe, and R.A. Williams, "Tea wastes as a low cost adsorbent for the removal of Cu and Pb from waste

water", Chemical Engineering Journal,vol.132, pp.299-309,2007.

[18]. M.K. Mondal, "Removal of Pb(II) ions from aqueous solution using activated tea waste: Adsorption on a fixed-bed column", Journal of Environmental Management,vol. 90,pp.3266-3271,2009.

[19]. B.H. Hameed, "Spent tea leaves: A new nonconventional and low-cost adsorbent for removal of basic dye from aqueous solutions", Journal of Hazardous Materials,vol.161,pp.753-759,2009.

[20]. E. Malkoc, and Y. Nuhoglu, "Investigation of Ni II removal from aqueous solutions using tea factory waste", Journal of Hazardous Materials,vol.127,pp.120-125,2005.

[21]. A.H. Mahavi, D. Naghipour, F. Vaezi, and S. Nazmara, "Tea waste as an adsorbent for heavy metal removal from industrial Waste waters", American Journal of Applied Sciences,vol.2,pp.372-375,2005.

[22]. W.C. Wanyonyi, J.M. Onyari, and P.M. Shiundu, "Adsorption of Methylene Blue dye from aqueous solutions using Eichhornia crassipes", Bulletin of Environmental Contamination and Toxicology,vol.91,pp.362-366,2013.

[23]. X. Xin, Q. Wei, J. Yang, L. Yan, R. Feng, G. Chen, B. Du, and H. Li, "Highly efficient removal of heavy metal ions by amine-functionalized mesoporous Fe_3O_4 nanoparticles", Chemical Engineering Journal,vol.184,pp.132-140,2012.

[24]. C. Chen, J. Hu, D. Shao, J. Li, and X. Wang, "Adsorption behavior of multiwall carbon nanotube/iron oxide magnetic composites for Ni(II) and Sr(II)", Journal of Hazardous Materials,vol.164,pp.923-928,2009.

[25]. H. Karami, "Heavy metal removal from water by magnetite nanorods", Chemical Engineering Journal,vol.219,pp.209-216,2013.

[26]. W. Konicki, I. Pełech, E. Mijowska, and I. Jasinska, "Adsorption of anionic dye Direct Red 23 onto magnetic multi-walled carbon nanotubes-Fe_3C nanocomposite: Kinetics, equilibrium and thermodynamics", Chemical Engineering Journal,vol.210,pp.87-95,2012.

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