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Removal of Cd(II) ion from wastewater by adsorption onto treated old newspaper: kinetic modeling and isotherm studies

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Abstract

Background: This paper studied the ability of using treated old newspaper (TNP) as synthetic adsorbent for the removal of Cd(II) from aqueous solutions by batch operation. Various operating parameters such as pH, initial metal ion concentration, adsorbent dosage, and equilibrium contact time have been studied.

Results: The results indicated that the adsorption of Cd(II) increased with the increasing pH, and the optimum solution pH for the adsorption of Cd(II) was found to be 6.4. Adsorption was rapid and occurred within 15 min for Cd(II) concentration range from 5 to 30 mg/L.

Conclusions: The kinetic process of Cd(II) adsorption onto TNP was found to fit the pseudo-second-order model. The equilibrium adsorption data for Cd(II) were better fitted to the Langmuir adsorption isotherm model.

Keywords: Kinetics, Equilibrium, Cadmium, Adsorption, Wastewater treatment, Newspaper pulp

Background

The removal of cadmium, Cd(II), ions is gaining wide interest from both environmental and economical viewpoints due to its serious hazardous impacts on humans, animals, and plants. There are several industries that are responsible for polluting the environment with high level of Cd(II) ions. The major sources of cadmium are products of industries such as metal plating, cadmium-nickel batteries, phosphate fertilizers, mining, pigments, stabilizers, metallurgy, ceramics, photograph, textile printing, lead mining, sewage sludge, alkaline batteries, and electroplating [1,2]. Conventional methods for heavy metal removal from wastewater include reduction, precipitation, ion exchange, filtration, electrochemical treatment, membrane technology, and evaporation, all of which may be ineffective or extremely expensive when metals are dissolved in large volumes of solution at relatively low concentrations [3,4]. Adsorption process is the most frequently applied method in industries for heavy metal removal. A lot of studies on this process have been carried out [5]. Many studies have recently devoted the usage of different adsorbent materials in processes involving the removal of Cd(II) ions from aqueous effluents with the aim of finding cheaper replacements for conventional sorbent material situations [6] such as activated carbon which is expensive for developing countries [7-10]. Therefore, many investigators have used inexpensive adsorbent materials, such as chitin [11], anaerobic sludge [12], apple residue [13], sawdust [14], rice polish [15], clay [16], zeolite [17], fly ash [18], chitosan [19], waste tea [20,21], seaweeds [22], and polyaniline coated on sawdust [23].

Used papers (old newspaper, old magazine, printed papers and mixed office waste paper) are an unavoidable form of domestic waste that keeps on accumulating steadily. Existing research into the use of treated old newspaper (TNP) as adsorbent for removing heavy metal ions from aqueous solution is extremely limited by Chakravarty et.al., who studied the use of TNP as adsorbent for the removal of zinc and copper [24,25]. This work studies the possibility of using old newspaper, a domestic waste, as an alternative low-cost sorbent in the removal of cadmium from aqueous solution and investigates the effect of initial Cd(II) concentration, contact time, dose, and pH on the adsorption process.

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Methods

Preparation of treated newspaper pulp

Old newspaper was treated with concentrated sodium bicarbonate solution for removing foreign materials like grease, black ink, and bleaching material (chlorine dioxide).

The newspaper pulp (NP) was washed several times with distilled water till the pH of the supernatant water layer of the pulp was around 6.5 to 7.0. A definite amount of air-dried newspaper pulp was then refluxed with 5.0% Na_2HPO_4 using a water condenser for 4 h to impregnate the phosphate into the cellulosic matrix. All the parameters such as the amount of NP, concentration of disodium hydrogen phosphate, and time were optimized for maximum impregnation. After phosphorylation, the pulp was again washed with distilled water till the solution was free from phosphate. The solution was cooled and gravity filtered through a Whatman 40 filter paper. The treated newspaper pulp was air-dried and finely ground with the help of a mixer grinder to make it fluffy [24].

Adsorbate solution

All solutions used in this study were prepared from cadmium chloride by weighting and dissolving the required amount in deionized water and using 1.0 N of NaOH and HCl for pH value adjustments.

Results and discussion

Characterization of TNP

The surface functional groups and structure were studied by Fourier transform infrared spectroscopy (FTIR). The FTIR spectra of NP and TNP were recorded between 300 and 4,000 cm^{-1} in FTIR-8400S (Shimadzu Corporation, Nakagyo-ku, Kyoto, Japan). The FTIR spectra showed a characteristic cellulose peak in the region of 1,000 to 1,200 cm^{-1}. The band near 1,300 cm^{-1} related to CH_2 wagging vibrations in the cellulose. The band near 3,300 cm^{-1} represented the OH vibrations. The 3,700-cm^{-1} band in NP was seen to be split into less intense peaks in TNP due to the change in intramolecular hydrogen bonding interactions. There was a band appearing in TNP at 1,000 cm^{-1}, corresponding to the P-O stretching (Figure 1).

Effect of contact time

In order to establish the equilibration time for maximum uptake and to determine the kinetics of the adsorption process, cadmium adsorption on TNP was investigated as a function of contact time, and the results are shown in Figure 2. Figure 2 shows that by increasing the initial concentration of cadmium, the amount of metal uptake is also increased. The contact time was maintained for an hour to ensure that equilibrium was really achieved. It is noticed from Figure 2 that the time to reach equilibrium is almost 15 min, and it is concentration-independent. In the initial stages, the removal efficiency of the metal ion by the TNP increased rapidly due to the abundant availability of active binding sites on the sorbent, and with gradual occupancy of these sites, the sorption became less efficient in the later stages [26].

Effect of TNP dosage

Figure 3 shows that the adsorption of cadmium on TNP decreased with the increasing adsorbent dosage. Cd adsorption capacity decreased gradually at the adsorbent dosage of 0.33 g with 8.41 mg/g adsorption capacity and at 1 g with 2.87 mg/g. These results may be due to the overlapping of adsorption sites as a result of adsorbent particle overcrowding [27]. Moreover, the high adsorbent dosage could impose a screening effect on the dense outer layer of the cells, thereby shielding the binding sites from metal [28].

Effect of pH

Hydrogen ion concentration in the adsorption is considered as one of the most important parameters that influence the adsorption behavior of metal ions in aqueous solution. It affects the solubility of the metal ions in the solution, replaces some of the positive ions found in the active sites, and affects the degree of ionization of the adsorbate during the reaction [29]. The effect of the initial pH on the sorption of Cd(II) ions onto TNP was evaluated within the pH range of 2 to 8. Studies beyond pH 8 were not attempted because precipitation of the ions as hydroxides would be likely to occur [30]. The effect of pH on the adsorption behavior of TNP for Cd(II) is shown in Figure 4. The initial pH of the solution significantly affected the adsorption capacity of adsorbent; adsorption capacity was highest when pH was 6.4 and decreased by either the raising or lowering of pH values under the present range of experimental condition. At lower values, the metal ion uptake was limited in this acidic medium, and this can be attributed to the presence of H^+ ions which compete with the Cd(II) ions for the adsorption sites. Contrarily, the metal ion was prone to $Cd(OH)_2$ deposition through hydrolysis at higher values of pH [31].

Adsorption isotherms

Langmuir isotherm

Langmuir proposed a theory to describe the adsorption of gas molecules onto metal surfaces. The Langmuir adsorption isotherm has found successful applications in many other real adsorption processes of monolayer adsorption. Langmuir's model of adsorption depends on the assumption that intermolecular forces decrease rapidly with distance and consequently predicts the

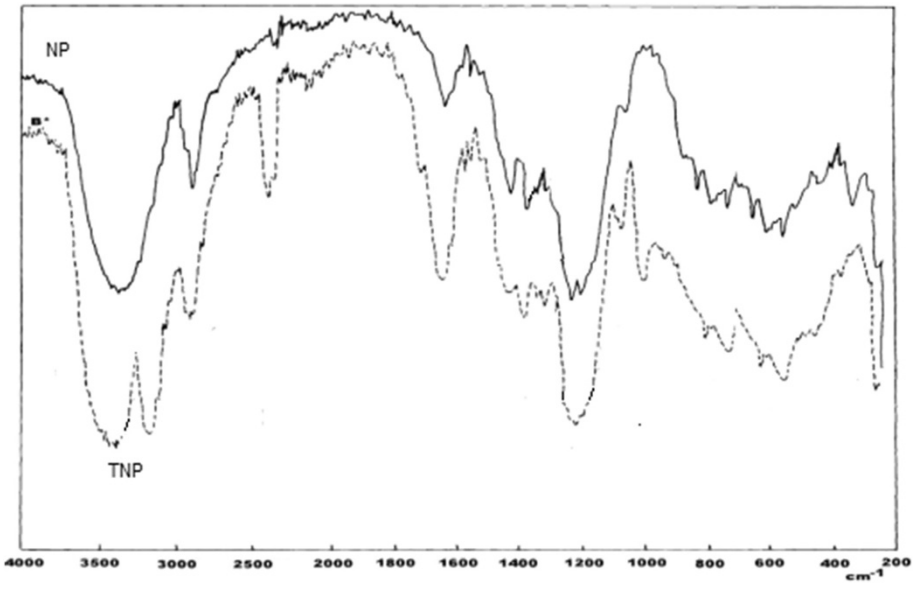

Figure 1 FTIR for NP and TNP.

existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The isotherm equation further assumes that adsorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a Cd(II) molecule occupies a site, no further adsorption can take place at that site. Moreover, the Langmuir equation is based on the assumption of a structurally homogeneous adsorbent where all adsorption sites are identical and energetically equivalent. Theoretically, the sorbent has a finite capacity for the sorbate. Therefore, a saturation value is reached beyond which no further adsorption can take place.

The experimental data were fitted to the Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{qb} + \frac{C_e}{q}, \tag{1}$$

where C_e (mg/L) is the equilibrium concentration of metal ion, q_e (mg/g) is the adsorption capacity in equilibrium state, q is the maximum adsorption capacity, and b is the Langmuir constant (equilibrium constant (L/mg)) which reflects quantitatively the affinity between TNP and Cd(II) ions (Figure 5). The affinity between Cd (II) and TNP adsorbent can be predicted using the

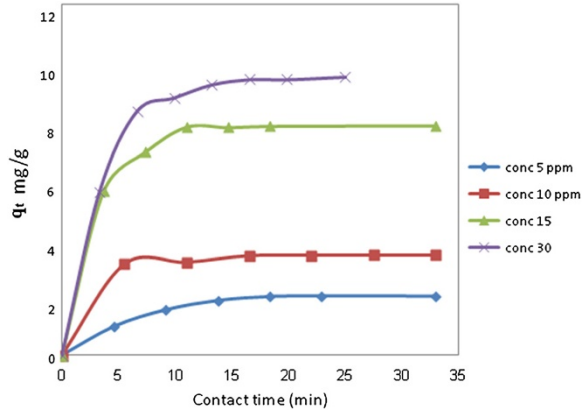

Figure 2 Effect of contact time on adsorption uptake of Cd(II) on TNP for different initial concentrations. Temperature is at 22°C, pH 6.4, and TNP dosage is 0.33 g/L.

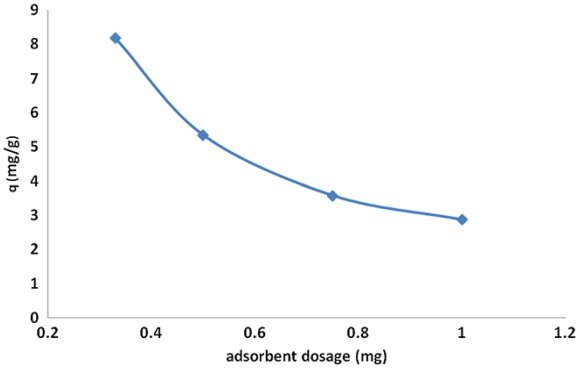

Figure 3 Effect of weight of adsorbent on adsorption of Cd(II) onto TNP. At pH 6.4, initial concentration of 30 mg/L, and TNP dosage from 0.33 to 1 g/L at 22°C.

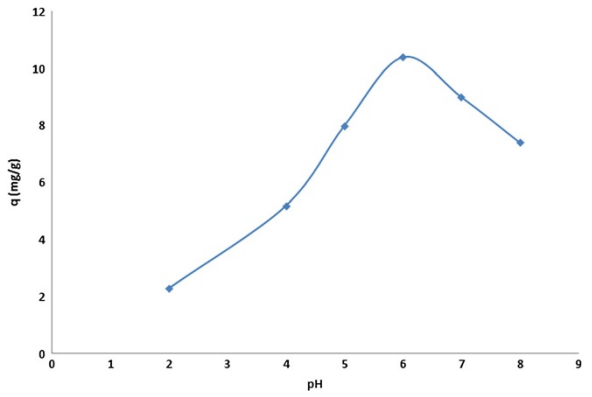

Figure 4 Effect of pH of the solution on adsorption of Cd(II) onto TNP. At an initial concentration of 30 mg/L and TNP dosage of 0.33 g/L at 22°C.

Langmuir parameter b from the dimensionless separation factor R_L [32]:

$$R_L = 1/(1 + bC_0), \quad (2)$$

where C_0 is the initial Cd(II) concentration, and b is Langmuir isotherm constant. The adsorption process as a function of R_L may be described as follows: $R_L > 1$ unfavorable, $R_L = 1$ linear, $0 < R_L < 1$ favorable, and $R_L = 0$ irreversible. The calculated R_L value for the adsorption of Cd(II) onto TNP was found to be 0.0235, which indicates a highly favorable adsorption of Cd(II) onto TNP.

Freundlich isotherm

The Freundlich adsorption equation has the following general form:

$$\ln q_e = \ln K_F + 1/n \ln C_e, \quad (3)$$

where K_F and n are the isotherm parameters to be determined. The Freundlich adsorption isotherm represents the relationship between the corresponding adsorption capacity q_e (mg/g) and the concentration of the metal in the solution at equilibrium C_e (mg/L) (Figure 6).

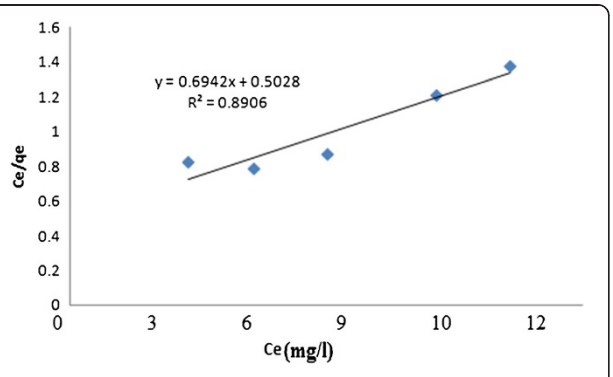

Figure 5 The Langmuir adsorption isotherm for Cd(II) adsorption onto TNP.

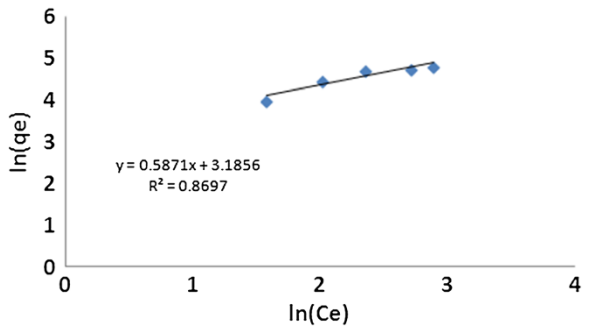

Figure 6 The Freundlich isotherm for Cd(II) adsorption onto TNP.

From Table 1, it is shown that both models of Langmuir isotherm and Freundlich isotherm have a narrow value of R^2 which varies from 0.8906 for Langmuir to 0.8697 for Freundlich. Thus, it is concluded that the Langmuir model is an appropriate model to represent the adsorption equilibrium data. The Freundlich constant n is found to be higher than 1, which indicates that the adsorption of Cd(II) on TNP is favorable.

Adsorption kinetics

Kinetics of adsorption is one of the most important characteristics that is responsible for the efficiency of adsorption. The adsorbate can be transferred from the solution phase to the surface of the adsorbent in several steps, and one or any combination of which can be the rate-controlling mechanism: (1) mass transfer across the external boundary layer film of liquid surrounding the outside of the particle, (2) diffusion of the adsorbate molecules to an adsorption site either by a pore diffusion process through the liquid-filled pores or by a solid surface diffusion mechanism, and (3) adsorption (physical or chemical) at a site on the surface (internal or external), and this step is often assumed to be extremely rapid.

Table 1 Fitted parameters of Cd(II) onto TNP adsorption system

Isotherm	Parameter	Value
Langmuir	q (mg/g)	1.4405
$q_c = \frac{q_{max} bC_e}{1+bC_e}$	b (L/mg)	1.38
	R^2	0.89
Freundlich	K_F mg/g (L.mg)$^{1/n}$	24.18
$q_e = k_F C_e^{1/n}$	$1/n$	0.5871
	R^2	0.87

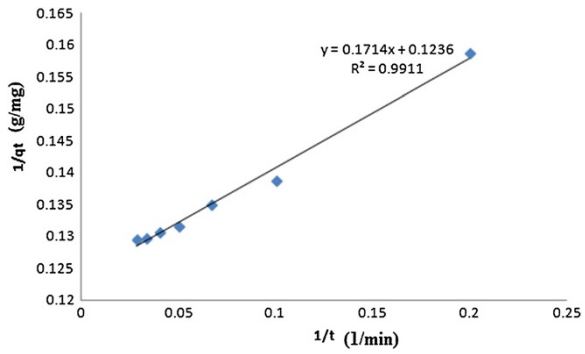

Figure 7 Fitting of pseudo-second-order model for Cd(II) adsorption onto TNP at 22°C, 0.33-g dosage, and pH 6.4.

The overall adsorption can occur through one or more steps. In order to investigate the mechanism of process and potential rate-controlling steps, the experimental kinetic data for the uptake of naphthalene at different initial concentrations, which is modeled by the pseudo-first order by Lagergren and the pseudo-second order by Ho and McKay [33], are given in Equations 4 and 5, respectively:

$$\log\ (q_e - q_t)\ = \log q_e - \frac{K_1}{2.303} t, \tag{4}$$

$$\frac{1}{q_t}\ =\ \frac{1}{k_{2q_e^2}}\ \frac{1}{t}\ +\ \frac{1}{q_6}. \tag{5}$$

The pseudo-first-order model was used to check the adsorption data of Cd(II) on TNP, but the correlation coefficient was not high. However, the pseudo-second -order kinetic model [33] was successfully applied with a very high correlation coefficient for explaining the kinetic data of the adsorption processes [34]. The adsorption of Cd(II) on TNP could be a pseudo-second order process rather than a first order.

By comparing the figures of the pseudo-first order (Figure 7) and the pseudo-second order (Figure 8)

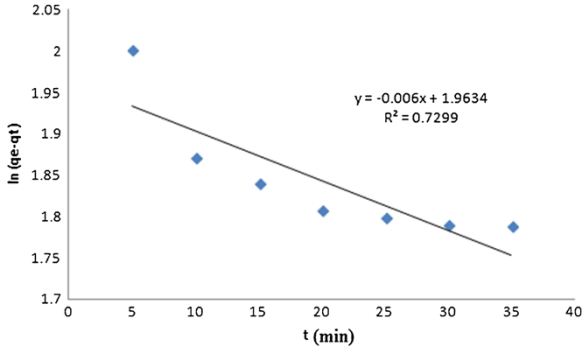

Figure 8 Fitting of Lagergren's pseudo-first-order model for Cd (II) adsorption on TNP at 22°C, 0.33-g dosage, and pH 6.4.

Table 2 Pseudo-second order at different initial Cd(II) concentrations

Cd (mg/L)	q_{exp} (mg/g)	q_e (mg/g)	K_1 (min^{-1})	R^2
5	2.61	2.8162	0.0145748	0.9975
10	3.88	3.41391	0.044268	0.9962
15	7.238	4.77566	0.032973	0.9984
30	9.00181	5.83948	0.089211	0.9911

At room temperature, dosage of 0.33 g, and pH 6.4.

models, it is obvious that the pseudo-second-order model fits the experimental data better than the pseudo-first order for the entire adsorption period. Also, from Table 2, the values of q_e obtained from the pseudo-second-order model are closer to the experimental results than q_e obtained from the pseudo-first-order model. By comparing the coefficient of determination R^2 in Tables 2 and 3, it is observed that the pseudo-second-order model fits the experimental data with higher R^2 values (0.9911 to 0.9975) than the pseudo-first order R^2 values (0.7299 to 0.7203). The higher R^2 values confirm that adsorption is well represented by the pseudo-second-order model.

Experimental

Adsorption kinetic experiments

Kinetic adsorption experiments were carried out to investigate the effect of time on the adsorption process and to identify the adsorption parameters. The experimental procedures were as follows:

1. A volume of 750 mL of cadmium chloride solution of various concentrations (5, 10, 15, and 30 mg/L) were prepared.
2. The cadmium chloride solution was placed in thermostatically controlled 2-L beaker, and 0.33 to 1 g of TNP was added to the solution and stirred by a rectangular impeller at a constant speed of 300 rpm for a definite shaking time varied between 0 and 30 min.
3. After shaking, the solution was allowed to settle for 30 min, filtered, and analyzed for cadmium by atomic absorption spectroscopy.

Table 3 Pseudo-first order at different initial Cd(II) concentrations

Cd (mg/L)	q_{exp} (mg/g)	q_e (mg/g)	K_2 (g/mg min)	R^2
5	2.61	2.27548	0.005716	0.7203
10	3.88	3.28342	0.0037681	0.72015
15	5.238	8.68386	0.006266	0.7240
30	7.12181	10.9502	0.006564	0.7299

At room temperature, dosage of 0.33 g, and pH 6.4.

4. The difference in the adsorbate (cadmium) content before and after adsorption represented the amount of adsorbate adsorbed by TNP.

The adsorption capacity (q) was calculated using the following formula:

$$q = \frac{C_0 - C}{W} \times V, \tag{6}$$

where C_0 is the initial concentration of metal ion in the solution (mg/L), C is the concentration of metal ion in solution (mg/L), V is the total volume of solution (L), and W is the TNP dosage (g).

Conclusions

The adsorption behavior of cadmium onto the TNP from aqueous solution has been investigated in this study. The present study shows that TNP can be used as low-cost adsorbent for the removal of cadmium from aqueous solution. The results suggest that The amount of cadmium removed changes with initial Cd(II) concentration and contact time. Maximum adsorption occurs at the Cd(II) concentration of 30 mg/L. The adsorption process increases with the increasing the pH value until it reaches 6.4 and then it decreases. The adsorption process increases with the increasing dose of TNP. The Langmuir and Freundlich isotherms can be used to describe the adsorption equilibria of cadmium onto TNP. It was found that the equilibrium adsorption data were more fitted to the Langmuir isotherm than to the Freundlich model. The kinetics of the adsorption were found to be fitted with pseudo-second-order model.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

MM carried out the experimental part, while MO carried out data interpretation and discussion. Both authors read and approved the final manuscript.

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MO got her B.Sc. and M.Sc. in Chemical Engineering from Alexandria University, Alexandria, Egypt. She received her Ph.D. from Wayne State University, Detroit, MI, USA. At present, she is an associate professor at the Petrochemical Engineering Department in Pharos University. MM got his B.Sc., M.Sc., and Ph.D. in Chemical Engineering from Alexandria University, Alexandria, Egypt. He is currently working as an assistant professor in the Chemical Engineering Department at Alexandria University.

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References

1. Patterson JW (1997) Industrial waste water treatment technology. Science Publishers, New York
2. Poon CPC (1986) Removal of cadmium from wastewaters. In: Mislin A, Ravero O (ed) Cadmium in the environment. Birkha User Verlag, Basel
3. Vole Sky B Biosorption of heavy metals. CRC Press, Boston, 408. 408
4. Basso MC, Cerrella EG, Cukierman AL (2002) Empleo de algas marinas para la biosorci´on de metales pesados de aguas contaminadas. Avances en Energías Renovables y Medio Ambiente 6:0329–5184
5. Rengaraj S, Yean KH, Kang SY, Lee JU, Kim KW, Moon SH (2002) Studies on adsorptive removal of Co(II), Cr(III) and Ni(II) by IRN77 cation-exchange resin. J Hazard Mater B92:185–198
6. Tamaki D, Ali R (2003) Study on removal of cadmium from water environment by adsorption on GAC, BAC and Biofilter. Ucd Dublin 8:35–39
7. Seco P, Marzal C, Gabaldon C, Aucejo A (1999) Effect of pH, cation concentration and sorbent concentration on cadmium and copper removal by a granular activated carbon. J Chem Technol Biotechnol 74(9):911–918
8. Marzal P, Seco A, Gabaldon C, Ferrer J (1996) Cadmium and zinc adsorption onto activated carbon influence of temperature pH and metal/carbon ratio. J Chem Tech Biotechnol 66(3):279–285
9. Seco A, Marzal P, Gabaldon C, Ferrer J (1997) Adsorption of heavy metals from aqueous solutions onto activated carbon in single Cu and Ni systems and in binary Cu–Ni, Cu–Cd and Cu–Zn systems. J Chem Tech Biotechnol 68(1):23–30
10. Rao MM, Ramesh A, Rao GP, Seshaiah K (2006) Removal of copper and cadmium from the aqueous solutions by activated carbon derived from *Ceiba pentandra* hulls. J Hazard Mater 129(1–3):123–129
11. Beguile B, Benaissa H (2002) Cadmium removal from aqueous solutions by chitin: kinetic and equilibrium studies. Water Res 36(10):2463–2474
12. Ulmanu ME, Marañón E, Fernández Y, Castrillón L, Anger I, Dumitriu D (2003) Removal of copper and cadmium ions from diluted aqueous solutions by low cost and waste material adsorbents. Water Air Soil Pollut 142(1–4):357–373
13. Lee SH, Jung CH, Chung H, Lee MY, Yang J (1998) Removal of heavy metals from aqueous solution by apple residues. Process Biochem 33:205–211
14. Shukla SS, Yu LJ, Dorris KL, Shuklab A (2005) Removal of nickel from aqueous solutions by sawdust. J Hazard Mater B 121:243–246
15. Singh KK, Rastogi R, Hasan SH (2005) Removal of cadmium from wastewater using agricultural waste 'rice polish'. J Hazard Mater A121:51–58
16. Farrah H, Pickering WF (1977) The sorption of lead and cadmium species by clay minerals. Aust J Chem 30:1417–1422
17. El-Kamash AM, Zaki AA, Abed El Geleel M (2005) Modeling batch kinetics and thermodynamics of zinc and cadmium ions removal from waste solutions using synthetic zeolite A. J Hazard Mater B 127:211–220
18. Al-Qodah Z (2006) Biosorption of heavy metal ions from aqueous solutions by activated sludge. Desalination 196:164–176
19. Jha IN, Iyengar L, Rae AVSP (1988) Removal of cadmium using chitosan. J Environ Eng 114:962–974
20. Orhan Y, Buyukgungor H (1993) The removal of heavy metals by using agricultural wastes. Water Sci Technol 28:247
21. Alhluwalia SS, Goyal D (2005) Removal of heavy metals by waste tea leaves from aqueous solution. Eng Life Sci 5(2):158
22. Costa DA, Franca FP (1996) Cadmium uptake by biosorbent seaweeds: adsorption isotherms and some process conditions. Sep Sci Technol 31:2373–239
23. Mansour MS, Ossman ME, Farag HA (2011) Removal of Cd (II) ion from waste water by adsorption onto polyaniline coated on sawdust. Desalination 272(1–3):301–305
24. Chakravarty S, Bhattacharjee S, Gupta KK, Singh M, Hema T, Chaturvedi S (2007) Maity, Adsorption of zinc from aqueous solution using chemically treated newspaper pulp. Bioresour Technol 98:3136–3141
25. Chakravarty S, Pimple S, Chaturvedi HT, Singh S, Gupta KK (2008) Removal of copper from aqueous solution using newspaper pulp as an adsorbent. J Hazard Mater 159:396–403
26. Costa ACA, Leite SGC (1991) Metal biosorption by sodium alginate immobilized *Chlorella homosphaera*. Biotechnol Lett 13:559–562
27. Garg VK, Gupta R, Yadav AB, Kumar R (2003) Dye removal from aqueous solution by adsorption on treated sawdust. Bioresour Technol 89:121–124

28. Pons MP, Fuste CM (1993) Uranium uptake by immobilized cells of *Pseudomonas* strain EPS 5028. Appl Microbiol Biotechnol 39:661–665
29. Nomanbhay SM, Palanisamy K (2004) Removal of heavy metals from industrial wastewater using chitosan coated oil palm shell charcoal. Electron J Biotechnol 8:43–53
30. Apiratikul R, Marhaba TF, Wattanachira S, Pavasant P (2004) Biosorption of binary mixtures of heavy metals by green macro alga *Caulerpa lentillifera*. J Sci Technol 26:199–207
31. Gode F, Pehlivan E (2003) A comparative study of two chelating ion-exchange resins for the removal of chromium (III) from aqueous solution. J Hazard Mater B 100:231–243
32. Weber TW, Chakravarty RK (1974) Pore and solid diffusion models for fixed bed adsorbers. Am Inst Chem Eng J 20:228–238
33. Ho YS, McKay G (2000) The kinetics of sorption of divalent metal ions onto sphagnum moss peat. Water Res 34(3):735–742
34. Ho YS (2003) Removal of copper ions from aqueous solution by tree fern. Water Res 37:2323–2330

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