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SORPTION OF HEAVY METAL IONS ON A GRANULAR BENTONITE–TYRE PYROLYSIS CARBON SORBENT: EFFECT OF pH, KINETICS, FIXED-BED DYNAMICS AND REGENERATION

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Abstract:

Waste tyres and metal-bearing industrial effluents are two linked environmental problems in mining regions. This study evaluated a granular sorbent made from bentonite and the carbon-containing residue of waste tyre pyrolysis (G-BU(opt), activated at 750 °C) for the removal of Fe(III), Cu(II), Zn(II), Ni(II), Pb(II), Cd(II) and Cr(VI) from aqueous solutions. Batch experiments examined the effect of initial pH (1.5–6.0), contact time (1–1440 min), temperature (293–323 K) and competition in an equimolar mixture; fixed-bed column tests and five sorption–desorption cycles were carried out with Cu(II). Cation removal increased from 6.24–18.53 % at pH 1.5 to 71.68–89.45 % at pH 6.0, which corresponds to 35.8–44.7 mg/g, whereas Cr(VI) removal reached a maximum of 34.56 % at pH 4.0. The pseudo-second-order model described the kinetics better than the pseudo-first-order model (adjusted R^2 of 0.9956–0.9991 and 0.9154–0.9513, respectively). Sorption was spontaneous ($\Delta G°$ from −2.57 to −3.94 kJ/mol) and endothermic ($\Delta H°$ from +5.36 to +6.09 kJ/mol). In the equimolar mixture the ratio of multi- to single-component uptake decreased in the order Pb(II) 0.86 > Cu(II) 0.77 > Zn(II) 0.69 > Cd(II) 0.67 > Ni(II) 0.65. In a 6 cm bed at 4 mL/min and C_0 = 100 mg/L, the Cu(II) breakthrough and exhaustion times were 15 and 65 min. After five regeneration cycles with 0.1 mol/L HCl the sorbent retained 75.38 % of its initial Cu(II) capacity.

Keywords: heavy metals; granular sorbent; tyre pyrolysis char; bentonite; sorption kinetics; thermodynamics; fixed-bed column; regeneration

Introduction

Heavy metals in mining and metallurgical effluents are persistent and toxic, and their removal is a standard requirement before discharge or reuse. Chemical precipitation, coagulation–flocculation, ion exchange, membrane filtration and electrochemical methods are all in use, and adsorption is attractive because it is simple to operate and can rely on inexpensive sorbents [1]. Carbon recovered from waste tyre pyrolysis is one such candidate. After KOH activation, tyre char removed Pb^{2+} with a capacity of 93.176 mg/g under optimised conditions [2], and even non-activated pyrolytic char removed more than 99 % of Pb, Ni, Cd and Co in another study [3].

In pyrolytic carbons and biochars, metal uptake usually involves several mechanisms at once: ion exchange, surface complexation, electrostatic attraction, precipitation and cation–π interaction [4]. The surface charge, characterised by the point of zero charge (pH_{pzc}), controls how cation and anion uptake depends on pH [5]. For practical use, equilibrium capacity alone is not enough; the uptake rate, temperature dependence, behaviour in a flow-through bed and the possibility of regenerating the sorbent also have to be known [6], [7].

Powdered carbon is difficult to separate from treated water, and flow-through adsorbers require granules. In a previous study, granules were prepared from bentonite and the carbon-containing material (CCM) obtained by pyrolysis of mining-vehicle tyres, and the effect of activation temperature on Fe(III) sorption was assessed [8]. The present work extends that study to several heavy metal ions. Its aim was to determine, for the granular sorbent obtained under the selected conditions, the effect of pH on the removal of seven metal species, the sorption kinetics and thermodynamics, competition in a multi-component solution, the fixed-bed behaviour and the stability of the sorbent over repeated regeneration cycles.

Materials and Methods

Sorbent and reagents

The sorbent (G-BU(opt)) consisted of granules made from bentonite and CCM by screw granulation and activated at 750 °C (the authors should specify which bentonite:CCM formulation was used). The CCM was produced by pyrolysis of end-of-life mining-vehicle tyres at 525–550 °C. Stock solutions (1000 mg/L) of Fe(III), Cu(II), Zn(II), Ni(II), Pb(II) and Cd(II) were prepared from the corresponding nitrates, and the Cr(VI) solution was prepared from $K_2Cr_2O_7$, all in distilled water; working solutions were obtained by dilution. Metal concentrations were determined by atomic spectrometry [9], and Cr(VI) was determined photometrically with diphenylcarbazide.

Batch experiments

The effect of pH was studied at C_0 = 100 mg/L, V = 50 mL and m = 0.1 g (2 g/L) at 25 °C, with agitation at 150 rpm for 24 h; the initial pH was varied from 1.5 to 6.0. Removal efficiency and uptake were calculated as

$$E = \frac{C_0 - C_e}{C_0} \cdot 100\ \%, \qquad q_e = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/L), V is the solution volume (L) and m is the sorbent mass (g).

For the kinetic experiments, 0.1 g of sorbent was added to 50 mL of solution at nominal concentrations of 50 and 100 mg/L and agitated at 25 °C for 1 to 1440 min, using a separate flask for every time point. The actual initial concentration of each series was measured and used in the calculations. The data were fitted by non-linear regression to the pseudo-first-order (PFO) [10] and pseudo-second-order (PSO) [11] models:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (2)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (3)$$

where q_t and q_e are the uptake at time t and at equilibrium (mg/g), and k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the rate constants. The models were compared by the adjusted coefficient of determination, R^2_{adj} [12].

Equilibrium experiments for the thermodynamic analysis were run in a thermostated shaker at 293, 303, 313 and 323 K for at least 24 h. The standard Gibbs energy, enthalpy and entropy changes were obtained from [13]

$$\Delta G^\circ = -RT\ln K_e^\circ, \qquad \ln K_e^\circ = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (4)$$

where K_e° is the dimensionless equilibrium constant, R is the gas constant and T is the absolute temperature. Competitive sorption was examined in an equimolar mixture containing 0.5 mmol/L each of Cu(II), Zn(II), Ni(II), Pb(II) and Cd(II), and the uptake of each metal was compared with its uptake from a single-component solution [14].

Fixed-bed column and regeneration

Column tests were performed in a glass column with an internal diameter of 1.5 cm at bed heights Z of 3, 6 and 9 cm, flow rates Q of 2, 4 and 6 mL/min and Cu(II) inlet concentrations of 50 and 100 mg/L. The breakthrough time t_b was taken at C_t/C_0 = 0.1 and the exhaustion time t_e at C_t/C_0 = 0.9. The length of the mass transfer zone was calculated as [6]

$$MTZ = Z\left(1 - \frac{t_b}{t_e}\right) \quad (5)$$

For regeneration, 0.1 g of Cu(II)-saturated sorbent was agitated with 50 mL of 0.1 mol/L HCl at 25 °C for 2 h, washed with distilled water to neutral pH, dried and reused. The procedure was repeated for five cycles. The relative efficiency in cycle n was calculated as $RE_n = q_n/q_1 \cdot 100\,\%$. The mass loss and mechanical strength of the granules were measured after each cycle.

Results

Effect of pH

At pH 1.5 the removal of all metals was low, between 6.24 % (Cd) and 18.53 % (Fe). Cation removal increased steadily with pH and reached 71.68 % for Cd(II) and 89.45 % for Pb(II) at pH 6.0 (Figure 1), which corresponds to uptakes of 35.8–44.7 mg/g. At pH 5.0 and 6.0 the removal decreased in the order Pb(II) > Cu(II) > Zn(II) > Ni(II) > Cd(II). Cr(VI) behaved differently: its removal was highest at pH 4.0 (34.56 %) and fell to 14.82 % at pH 6.0.

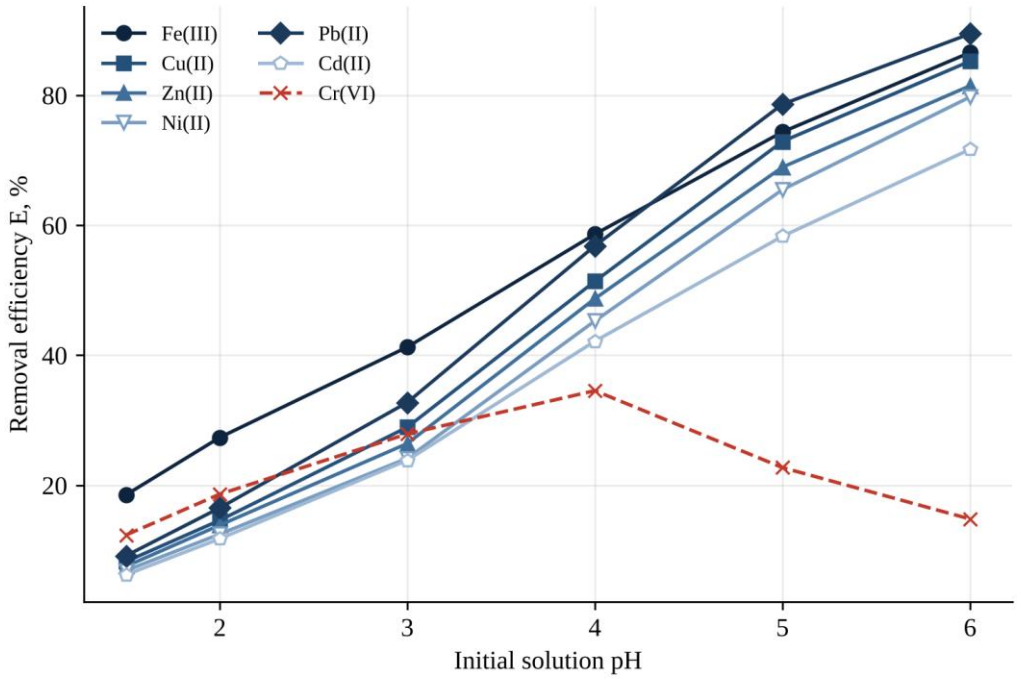


Figure 1. Effect of initial pH on the removal of metal ions by G-BU(opt) (C_0 = 100 mg/L, sorbent dose 2 g/L, 25 °C, 24 h).

Sorption kinetics

The kinetic parameters are listed in Table 1. For all four metals the PSO model gave a better fit (R^2_{adj} = 0.9956–0.9991) than the PFO model (0.9154–0.9513). The PSO model overestimated the experimental q_e by 2.0–2.6 %, and the PFO model underestimated it by 8.8–9.7 %. When C_0 was raised from 50 to 100 mg/L, k_2 decreased by 26–31 %; for Cu(II), for example, it fell from 0.00287 to 0.00197 g mg⁻¹ min⁻¹.

Table 1. Parameters of the pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models (G-BU(opt), 25 °C, 2 g/L)

			PFO model			PSO model		
Metal	**C_0, mg/L**	**$q_{e,exp}$, mg/g**	**q_e, mg/g**	**k_1, min⁻¹**	**R^2_{adj}**	**q_e, mg/g**	**k_2, g mg⁻¹ min⁻¹**	**R^2_{adj}**
Fe(III)	50	24.53	22.37	0.0451	0.9452	25.16	0.00253	0.9981
Fe(III)	100	48.57	44.12	0.0384	0.9327	49.83	0.00186	0.9974
Cu(II)	50	23.84	21.56	0.0423	0.9385	24.31	0.00287	0.9986
Cu(II)	100	46.92	42.71	0.0359	0.9253	48.14	0.00197	0.9968
Pb(II)	50	25.61	23.14	0.0482	0.9513	26.27	0.00234	0.9991
Pb(II)	100	50.24	45.37	0.0406	0.9417	51.52	0.00173	0.9983
Ni(II)	50	21.43	19.38	0.0404	0.9286	21.95	0.00312	0.9972
Ni(II)	100	42.36	38.27	0.0337	0.9154	43.48	0.00224	0.9956

Note: C_0 is the nominal initial concentration; $q_{e,exp}$ was calculated from the initial concentration measured in each series.

Thermodynamics and competitive sorption

Between 293 and 323 K, ΔG° was negative for all three metals studied: from −2.84 to −3.68 kJ/mol

for Fe(III), from −2.57 to −3.45 kJ/mol for Cu(II) and from −3.07 to −3.94 kJ/mol for Pb(II). The corresponding K_e° values increased from 3.21 to 3.94, from 2.87 to 3.62 and from 3.53 to 4.33. ΔH° was positive (+5.39, +6.09 and +5.36 kJ/mol for Fe(III), Cu(II) and Pb(II)), ΔS° ranged from +28.1 to +29.6 J/(mol·K), and the van't Hoff plots had R^2 = 0.9996–0.9999.

In the equimolar mixture, the uptake of every metal was lower than in its single-component solution. The ratio q_{mix}/q_{single} was 0.86 for Pb(II), 0.77 for Cu(II), 0.69 for Zn(II), 0.67 for Cd(II) and 0.65 for Ni(II).

Fixed-bed column and regeneration

When the bed height was increased from 3 to 9 cm (Q = 4 mL/min, C_0 = 100 mg/L), t_b rose from 4 to 32 min, t_e from 18 to 132 min and the MTZ from 2.33 to 6.82 cm. Increasing the flow rate from 2 to 6 mL/min at Z = 6 cm shortened t_b from 43 to 6 min and t_e from 172 to 26 min. Under the reference conditions (Z = 6 cm, Q = 4 mL/min, C_0 = 100 mg/L), t_b was 15 min, t_e was 65 min and the MTZ was 4.62 cm; lowering C_0 to 50 mg/L extended t_b to 21 min and t_e to 88 min.

Over five sorption–desorption cycles the Cu(II) uptake decreased from 25.63 to 19.32 mg/g (RE_5 = 75.38 %). Over the same cycles the desorption efficiency fell from 96.57 to 71.26 %, the mechanical strength from 99.23 to 87.24 %, and the cumulative mass loss reached 8.54 % (Figure 2).

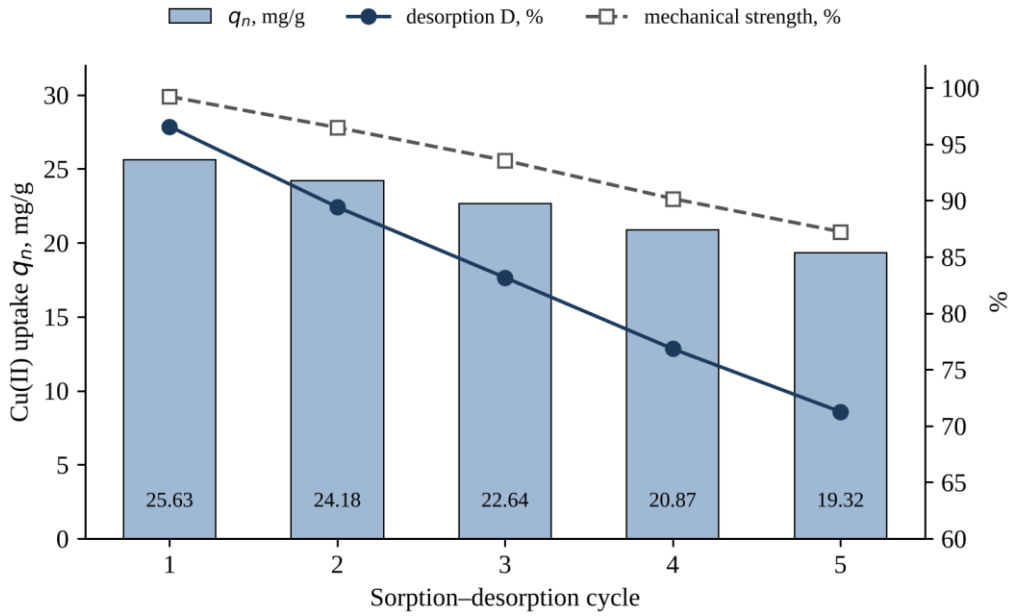


Figure 2. Cu(II) uptake, desorption efficiency and mechanical strength of G-BU(opt) over five regeneration cycles with 0.1 mol/L HCl.

Discussion

The low cation uptake at pH 1.5 is explained by protonation of the surface and by competition between H^+ and metal cations for the same sites; as pH rises, deprotonation makes the surface negatively charged and favours cation uptake. In the bentonite–CCM composite two further factors operate. Montmorillonite carries a permanent negative charge from isomorphous substitution and can exchange cations even below pH_{pzc}, while calcium carbonate present in the CCM dissolves and raises the solution pH. For this reason, the values obtained for Cu(II) and Pb(II) at pH 5–6, and for Fe(III) above pH 3, may include a contribution from hydroxide precipitation; the Fe(III) values in that range were therefore not interpreted as sorption capacities. The decrease of Cr(VI) removal at higher pH agrees with electrostatic repulsion of chromate anions from a negatively charged surface. The lower values at pH 1.5–3.0 may be related to the speciation of Cr(VI) or to its partial reduction to Cr(III), and this needs a separate study.

The order Pb > Cu > Zn > Ni > Cd observed at pH 5–6 was obtained at equal mass concentrations (100 mg/L), which correspond to different molar concentrations (0.48 mmol/L for Pb and 1.57 mmol/L for Cu). Selectivity was therefore judged from the equimolar experiment. Under competition, Pb(II) lost the least capacity (14 %) and Ni(II) the most (35 %), and Cd(II) moved above Ni(II). This shows that the metals compete for at least part of the active sites.

A better fit of the PSO model does not by itself prove chemisorption, so it is treated here only as the more suitable empirical description. The decrease in k_2 at higher C_0 is consistent with stronger competition for surface sites. Among the thermodynamic parameters, ΔH° does not depend on multiplying the equilibrium constant by a constant factor, whereas the absolute values of ΔG° and ΔS° depend on how the constant is made dimensionless. The discussion therefore relies mainly on the signs and trends: sorption is spontaneous and endothermic, and it becomes more favourable at higher temperature. No conclusion about the physical or chemical nature of sorption was drawn from the magnitude of ΔH°.

The column results follow the expected pattern, with longer breakthrough and exhaustion times in taller beds and shorter times at higher flow rates. At Z = 3–9 cm the MTZ-to-bed-height ratio stayed almost constant (0.76–0.78), meaning that most of the bed operated within the mass transfer zone under the tested conditions. Taller beds and lower flow rates would therefore be needed in a practical adsorber. During regeneration the uptake fell by 1.58 mg/g per cycle on average, which indicates that part of the metal is retained irreversibly and that the granules wear mechanically. Even so, three quarters of the initial capacity remained after five cycles, so the sorbent can be reused several times.

This study has several limitations. The contribution of each sorption mechanism was not quantified; samples before and after sorption should be examined by XRD, IR spectroscopy and SEM-EDS for that purpose. pH_{pzc} of the granules was not determined, and the final solution pH values are not reported here, so the share of precipitation could not be separated from sorption. Column and regeneration tests were limited to Cu(II).

Conclusions

A granular sorbent produced from bentonite and waste tyre pyrolysis carbon removed heavy metal cations increasingly with pH, from 6.2–18.5 % at pH 1.5 to 71.7–89.5 % at pH 6.0; Cr(VI) removal peaked at pH 4.0 (34.6 %). The kinetics were described better by the pseudo-second-order model (R^2_{adj} = 0.9956–0.9991), and between 293 and 323 K sorption was spontaneous and endothermic (ΔH° = +5.36 to +6.09 kJ/mol). In an equimolar mixture the selectivity order was Pb(II) > Cu(II) > Zn(II) > Cd(II) > Ni(II). In a 6 cm bed at 4 mL/min the Cu(II) breakthrough and exhaustion times were 15 and 65 min, and after five regeneration cycles with 0.1 mol/L HCl the sorbent kept 75.38 % of its capacity. These results support the use of tyre pyrolysis carbon, combined with local bentonite, as a reusable granular sorbent for treating metal-bearing effluents.

References

[1] F. Fu and Q. Wang, “Removal of heavy metal ions from wastewaters: A review,” *J. Environ. Manage.*, vol. 92, no. 3, pp. 407–418, 2011, doi: 10.1016/j.jenvman.2010.11.011.

[2] H. Rutto, T. Seidigeng, and L. Malise, “Adsorption of lead ions onto chemically activated carbon from waste tire char and optimization of the process using response surface methodology,” *Arch. Environ. Prot.*, vol. 45, no. 4, pp. 92–103, 2019, doi: 10.24425/aep.2019.130245.

[3] S. M. H. Shah *et al.*, “Mechanistic insights into heavy metal adsorption on pyrolytic char from waste tires using experimental and DFT approaches,” *Discover Water*, vol. 5, no. 1, Art. no. 107, 2025, doi: 10.1007/s43832-025-00314-x.

[4] M. I. Inyang *et al.*, “A review of biochar as a low-cost adsorbent for aqueous heavy metal removal,” *Crit. Rev. Environ. Sci. Technol.*, vol. 46, no. 4, pp. 406–433, 2016, doi: 10.1080/10643389.2015.1096880.

[5] B. M. Babić, S. K. Milonjić, M. J. Polovina, and B. V. Kaludierović, "Point of zero charge and intrinsic equilibrium constants of activated carbon cloth," *Carbon*, vol. 37, pp. 477–481, 1999, doi: 10.1016/S0008-6223(98)00216-4.
[6] H. Patel, "Fixed-bed column adsorption study: a comprehensive review," *Appl. Water Sci.*, vol. 9, no. 3, Art. no. 45, 2019, doi: 10.1007/s13201-019-0927-7.
[7] S. Lata, P. K. Singh, and S. R. Samadder, "Regeneration of adsorbents and recovery of heavy metals: a review," *Int. J. Environ. Sci. Technol.*, vol. 12, no. 4, pp. 1461–1478, 2015, doi: 10.1007/s13762-014-0714-9.
[8] Sh. T. Jo'rayev, "Technologies for obtaining and applying ingredients based on low-temperature thermal processing of vulcanized rubber industry waste," D.Sc. dissertation, Navoi State Univ. of Mining and Technologies, Navoi, Uzbekistan, 2025 (in Uzbek).
[9] *Drinking Water. Determination of Elements Content by Atomic Spectrometry Methods*, GOST 31870-2012, 2012 (in Russian).
[10] S. Lagergren, "Zur Theorie der sogenannten Adsorption gelöster Stoffe," *Kungliga Svenska Vetenskapsakademiens Handlingar*, vol. 24, no. 4, pp. 1–39, 1898.
[11] Y. S. Ho and G. McKay, "Pseudo-second order model for sorption processes," *Process Biochem.*, vol. 34, no. 5, pp. 451–465, 1999, doi: 10.1016/S0032-9592(98)00112-5.
[12] J.-P. Simonin, "On the comparison of pseudo-first order and pseudo-second order rate laws in the modeling of adsorption kinetics," *Chem. Eng. J.*, vol. 300, pp. 254–263, 2016, doi: 10.1016/j.cej.2016.04.079.
[13] E. C. Lima, A. Hosseini-Bandegharaei, J. C. Moreno-Piraján, and I. Anastopoulos, "A critical review of the estimation of the thermodynamic parameters on adsorption equilibria. Wrong use of equilibrium constant in the Van't Hoof equation for calculation of thermodynamic parameters of adsorption," *J. Mol. Liq.*, vol. 273, pp. 425–434, 2019, doi: 10.1016/j.molliq.2018.10.048.
[14] H. N. Tran, S.-J. You, A. Hosseini-Bandegharaei, and H.-P. Chao, "Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: A critical review," *Water Res.*, vol. 120, pp. 88–116, 2017, doi: 10.1016/j.watres.2017.04.014.