

Kinetics Investigation of Cr(VI) Removal by Modified Perlite with Fe₂O₃ and MnO₂ Nanomaterials

Serpil Edebali

Abstract—Novel nanocomposite adsorbents for Cr(VI) removal from aqueous solution were synthesized by modifying perlite with α -MnO₂ and γ -Fe₂O₃ nanoparticles. Nanocomposite adsorbents were characterized using Scanning Electron Microscopy (SEM) and FTIR. The adsorption capacity for Cr(VI) was found to be highly pH dependent and the adsorption kinetics followed the pseudo-second order kinetic model when compared to first-order kinetic model. The adsorption capacity was 8.64 and 7.6 mg g⁻¹ for γ -Fe₂O₃ and α -MnO₂ containing adsorbents as compared to very low adsorption capacity for perlite alone, confirming that these composites retain the constituent nanomaterial properties while being macroscopic particles suitable for chromium removal in water treatment.

Index Terms—Nanomaterials, Cr(VI), modification, perlite.

I. INTRODUCTION

Technological developments and industrialization have a contribution to comfortable lives of people as well as cause important environmental problems. Presence of heavy metals in the environment is very important for human beings and living things in terms of their toxicity. It becomes a health problem when high concentrations of heavy metals directly or indirectly contact with agricultural areas, underground water sources, humans and animals. All over the world, discharged wastewater of industrial activities include heavy metals such as copper, nickel, arsenic, chromium, lead, mercury, etc.

Among these heavy metals, chromium and its compounds are extensively used in electroplating, leather tanning, metal finishing, nuclear power plant, dyeing, photography industries and textile industries [1], [2]. In aqueous solution Cr exists both in trivalent (Cr(III)) and hexavalent (Cr(VI)) forms. Trivalent chromium is considered as an essential micronutrient for human, plant and animal metabolism and less toxic than Cr(VI) which is extremely mobile in the environment and very toxic, carcinogenic and mutagenic to living organism.

This is the first time perlite modified with α -MnO₂ and γ -Fe₂O₃ nanocomposites have been used as effective sorbents with enhanced capacity for Cr(VI) removal.

II. MATERIALS AND SYNTHESIS

All chemicals were reagent grade and they were used

without further purification. Sodium hydroxide (NaOH, 98%) and HCl from Merck, nanomaterials from Sigma. The expanded perlite, which is a chemically and thermally modified natural perlite and is used as a soil additive, was obtained from Turkish company. Stock solution (1000 mg/L) of Cr(VI) was prepared by dissolving K₂Cr₂O₇ in deionised water. All other chemicals used in this study were of analytical grade and were freshly distilled before use. The Cr(VI) solutions of required concentrations for further experiments were made by diluting the stock and adjusting the pH with HCl.

For the synthesis of perlite/ γ -Fe₂O₃ composite, 0.5 g of γ -Fe₂O₃ nanoparticles and 1 g of expanded perlite powder were suspended in 30 mL of a water:ethanol (1:1, v/v) solution and homogenized for 6 h. After that the sample was kept overnight in a glass flask at room temperature to allow the sample to settle down. The liquid was discarded and the settlement was dried at 80 °C for 12 h, thus obtaining the composite denoted as PI.

In addition to this, to synthesize perlite/ α -MnO₂ composite, perlite (P) and α -MnO₂ powder blend (2:1 w/w) was first gently mixed in a 20 mL water:ethanol (1:1, v/v) solution using a glass rod. After that, 10 mL of the solution was placed into each of two grinding jars and ground at a frequency of 20 Hz for 2 h. The sample was then kept overnight in a glass flask at room temperature, allowing the particles to settle down. The liquid part was discarded and the settlement was dried at 80 °C for 12 h, thus obtaining the composite, further denoted as PM [1].

All experiments were conducted in a 100 mL bottles placed on a shaker (200 rpm) at room temperature. The pH of the solution was manually maintained at the desired value using 0.1 M HCl and 0.1 M NaOH. The pH was readjusted when necessary by addition of the acid or the base.

III. RESULTS AND DISCUSSION

A. Effect of Adsorbent Dosage

First of all, effect of adsorbent dosage on the removal of Cr(VI) by nanocomposite materials was investigated and the results are indicated in Fig. 1(a) and Fig. 1(b).

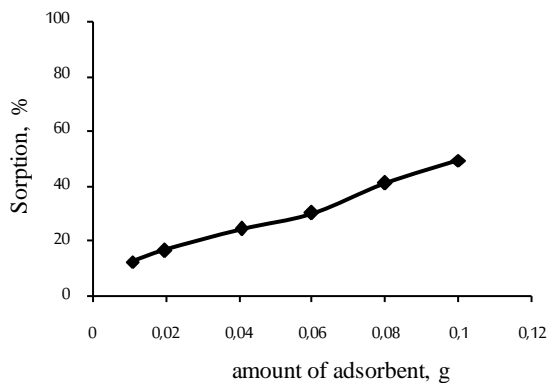
It can be seen that Cr(VI) percentage removal increases with an increase in nanocomposite dosages. Specifically, the extent of Cr(VI) removal from 25 mL of 20 mg/L Cr(VI) solution, changes from 12.7% at a dose of 0.01 g to 52.% at a dose 0.10 g of PI and from 13.9% to 48.0% with the same amounts of PM. The increase in the amount of the nanocomposites is significantly influenced the extent of adsorption due to the increase in the number of active sites

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Serpil Edebali is with Selcuk Univeristy, Faculty of Engineering, Chemical Engineering Department, 42075, Konya, Turkey (e-mail: serpilcetin@gmail.com).

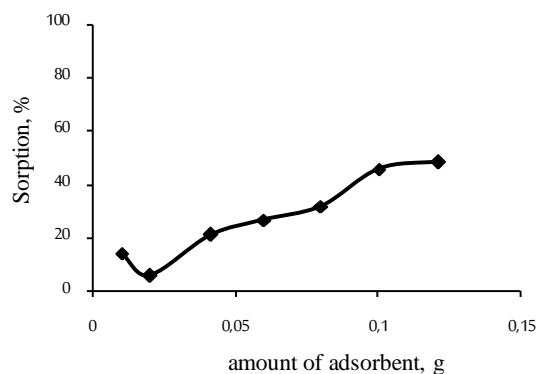
available for adsorption. Similarly, in the study where the effect of adsorbent dose on Cr(VI) removal was investigated by Zhang *et al.* (2010), it was found that 4 g/L was required to achieve 100% removal of Cr(VI) from aqueous solution containing 50 mg/L [2].

PI



(a)

PM



(b)

Fig. 1. Effect of adsorbent dosage on the removal of Cr(VI) (a) PI, (b) PM.

B. Effect of Contact Time

The contact time was varied from 5 to 180 min for the adsorption of Cr(VI) by the nanocomposites. The effect of contact time on the adsorption of Cr(VI) is shown in Fig. 2(a) and Fig. 2(b). The adsorption of Cr(VI) increased with increasing contact time and attained an optimum at about 60 min for both nanocomposite adsorbents. High adsorption rates of chromium for them are observed at the onset, and then plateau values are reached.

C. Effect of pH

In the sorption studies, pH is the first important factor for the quantitative recoveries of analytes. Since Cr(VI) speciation in aqueous solutions is highly dependent on the pH of the solution, the influences of solution pH on the recoveries of Cr(VI) by the resins were investigated in the pH range of 1–5 (Fig. 3) by using 0.1 M of HCl and NaOH solutions. Cr(VI) was quantitatively recovered more at low pH values and as the values of pH were increased, the recovery values for Cr(VI) decreased.

D. Sorption Kinetics

After investigating the effect of contact time on the Cr(VI)

adsorption, to understand the kinetic mechanism of the present adsorption process, pseudo-first-order and pseudo-second-order models were used to fit the kinetic data [3]–[6]. The linearized forms of the pseudo-first order and pseudo-second-order equations are given in Equations (1) and (2), respectively.

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_{ad}t}{2.303}\right) \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_e}\right)t \quad (2)$$

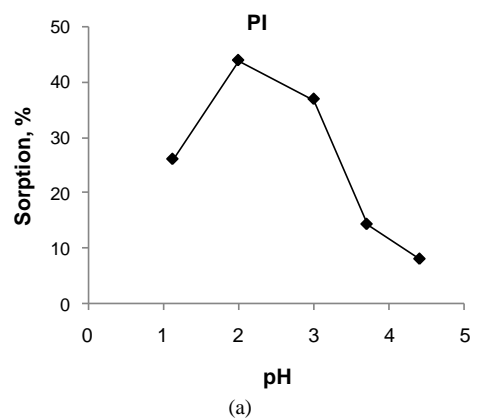
where q_t is Cr(VI) uptake at time t , and k_1 and k_2 are the pseudo first order and second order rate constants, respectively. From pseudo second kinetic model, the initial sorption rate, h_0 (mg/g/min) can be defined as [7]:

$$h_0 = k_2 q_e^2 (t \rightarrow 0) \quad (3)$$

The linearized plots of Eq. (1) and Eq. (2) are shown in Fig. 4a and Fig. 4b, Fig. 5a and Fig. 5b, respectively. From the plots, the rate constants together with the correlation coefficients were calculated and determined (see Table I).

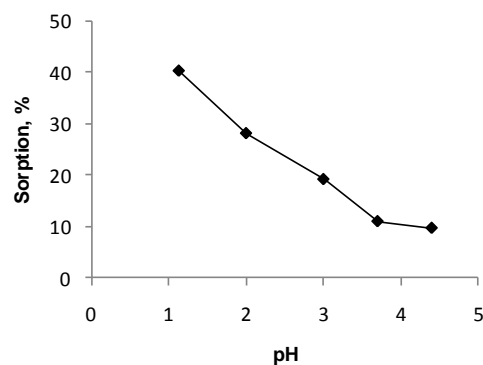
TABLE I: KINETIC PARAMETERS OF Cr(VI) REMOVAL ONTO PERLITE/B-MNO₂ AND PERLITE/A-FE₂O₃ NANOCOMPOSITES

| | Pseudo-first-order model | | | Pseudo-second-order model | | |
|----|--------------------------|-------|-------|---------------------------|-------|-------|
| | K_1 | q_e | R^2 | K_2 | q_e | R^2 |
| PM | 0.00014 | 35.5 | 0.76 | 0.037 | 1.43 | 0.99 |
| PI | 0.00012 | 34.7 | 0.78 | 0.159 | 1.02 | 0.98 |



(a)

PM



(b)

Fig. 2. Effect of pH on the removal of Cr(VI) (a) PI, (b) PM.

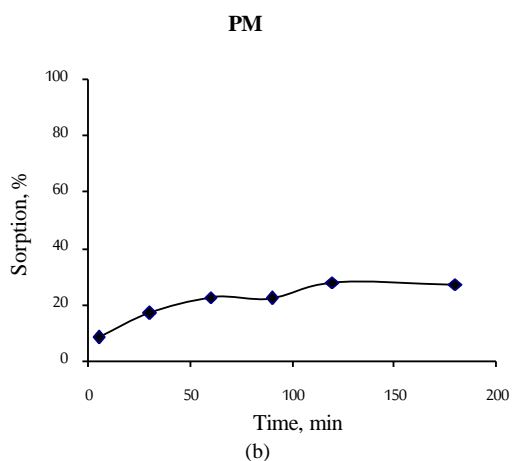
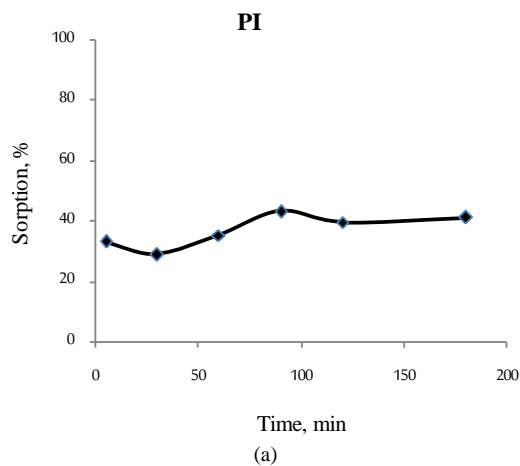


Fig. 3. Effect of time on the removal of Cr(VI) by (a) PI, (b) PM.

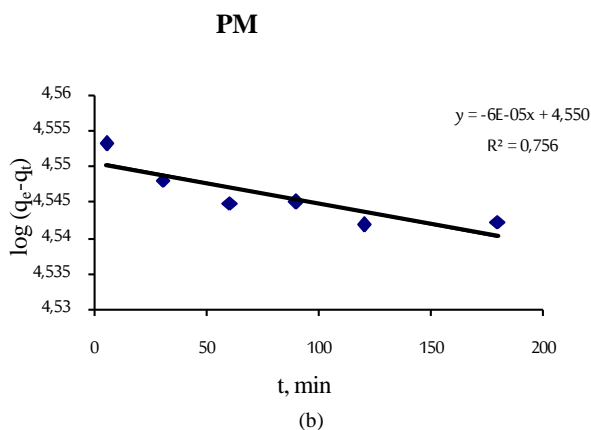
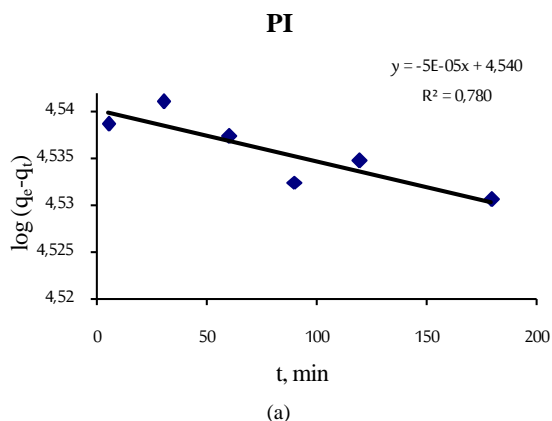


Fig. 4. Pseudo-first-order kinetics model for (a) PI, (b) PM.

Adsorption compared to pseudo-first-order model ($R^2 \approx 0.756-0.780$) for both nanocomposites.

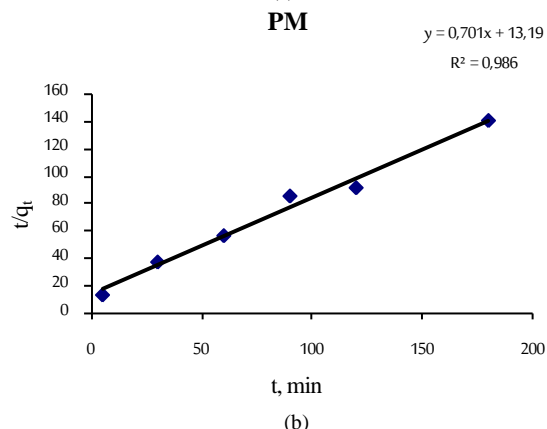
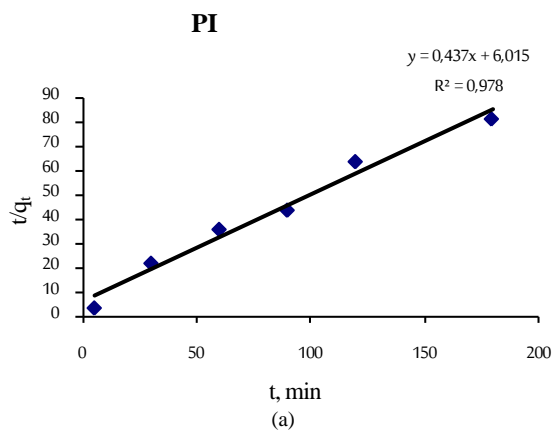


Fig. 5. Pseudo-second-order kinetics model for (a) PI, (b) PM.

From the values of the correlation coefficients, the pseudo-second-order model ($R^2 \approx 0.978-0.986$) gave better description of the Cr(VI).

IV. CONCLUSION

In our study, it was found that pseudo-second order kinetic model was appropriate to explain the kinetic behaviour of both nanocomposites. In the study of Gupta and Babu (2009), the results for removal of Cr(VI) metal were tested by pseudo-first order, pseudo-second order and Elovich kinetic models and finally pseudo-second order kinetic model was also the most suitable model for the removal of Cr(VI). Moreover, Azizian (2004) emphasized that general equation was well fitted to pseudo-first order kinetic model for high initial concentrations while pseudo-second order kinetic model was more suitable for lower initial concentrations. On the other hand, Rengaraj *et al.*, (2001) found that pseudo-first order kinetic model was used to explain the adsorption of ions from aqueous solutions when a single type was thought on a heterogeneous surface [8].

REFERENCES

- [1] D. N. Thanh, M. Singh, P. Ulbrich, N. Strnadova, and F. Štepanek, "Perlite incorporating β -Fe₂O₃ and α -MnO₂ nanomaterials: Preparation and evaluation of a new adsorbent for As(V) removal," *Sep. Purif. Technol.*, vol. 82, pp. 93-101, 2011.
- [2] R. Zhang, H. Ma, and B. Wang, "Removal of chromium(VI) from aqueous solution using polyaniline doped with sulfuric acid," *Ind. Eng. Chem. Res.* vol. 49, pp. 9998-10004, 2010.
- [3] M. Bhaumik, A. Maity, V. V. Srinivasu, and M. S. Onyango, "Enhanced removal of Cr(VI) from aqueous solution using

- polypyrrole/Fe₃O₄ magnetic nanocomposite," *J. Hazard. Mater.* vol. 190, pp. 381–390, 2011.
- [4] A. Saeid, "Kinetic models of sorption: A theoretical analysis," *J. Colloid Interf. Sci.*, vol. 276, pp. 47–52, 2004.
- [5] Y. S. Ho and G. McKay, "The kinetics of sorption of divalent metal ions onto sphagnum moss peat," *Water Res.*, vol. 34, no. 3, pp. 735–742, 2000.
- [6] I. A. Rauf, B. H. Nawaz, H. M. Asif, and N. Razyia, "Kinetic and thermodynamic aspects of Cu(II) and Cr(III) removal from aqueous solutions using rose waste biomass," *J. Hazard. Mater.*, vol. 161, pp. 941–947, 2009.
- [7] G. Suresh and B. V. Babu, "Removal of toxic metal Cr(VI) from aqueous solutions using saw dust as adsorbent: Equilibrium, kinetics and regeneration studies," *Chem. Eng. J.*, vol. 150, pp. 352–365, 2009.
- [8] S. Rengaraj, K. H. Yeon, and S. H. Moon, "Removal of chromium from water and wastewater by ion exchange resins," *J. Hazard. Mater.*, vol. B87, pp. 273–287, 2001.



Serpil Edeballi was born in Konya, Turkey, in 1977. She received the B.S. degree in Food Engineering Department of METU in Ankara. Then she received the MSc and PhD degrees in chemical engineering from Selcuk University of Konya in 2004 and 2010, respectively.

From 2002 to 2013, she was a research assistant in Chemical Engineering Department of Selcuk University. Since 2013, she has been an assistant professor with the same department. She gives lectures in the subjects of heat transfer and fluid mechanics. Her research interests include wastewater treatment, removal of heavy metals and dyes, synthesis of nanoparticles and applications, sorption processes with resins and membrane as well as membrane-adsorption hybrid systems. She has duties as a researcher in various COST and FP7 projects.