

Supporting Information

Novel synthesis of clay supported amorphous aluminum nanocomposite and its application in removal of hexa-valent Chromium from aqueous solutions

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Cr(VI) sorption was studied as a function of increasing sorbent amount (constant volume- 25ml) to optimize the amount of B-Al nanocomposite for further sorption experiments. As shown in fig. S1, as amount of B-Al composite increased, sorption capacity decreased drastically which was due to complete removal (>99%) by 15 mg of the composite. Hence the amount of B-Al to be used for further sorption experiments was decided to be 15 mg.

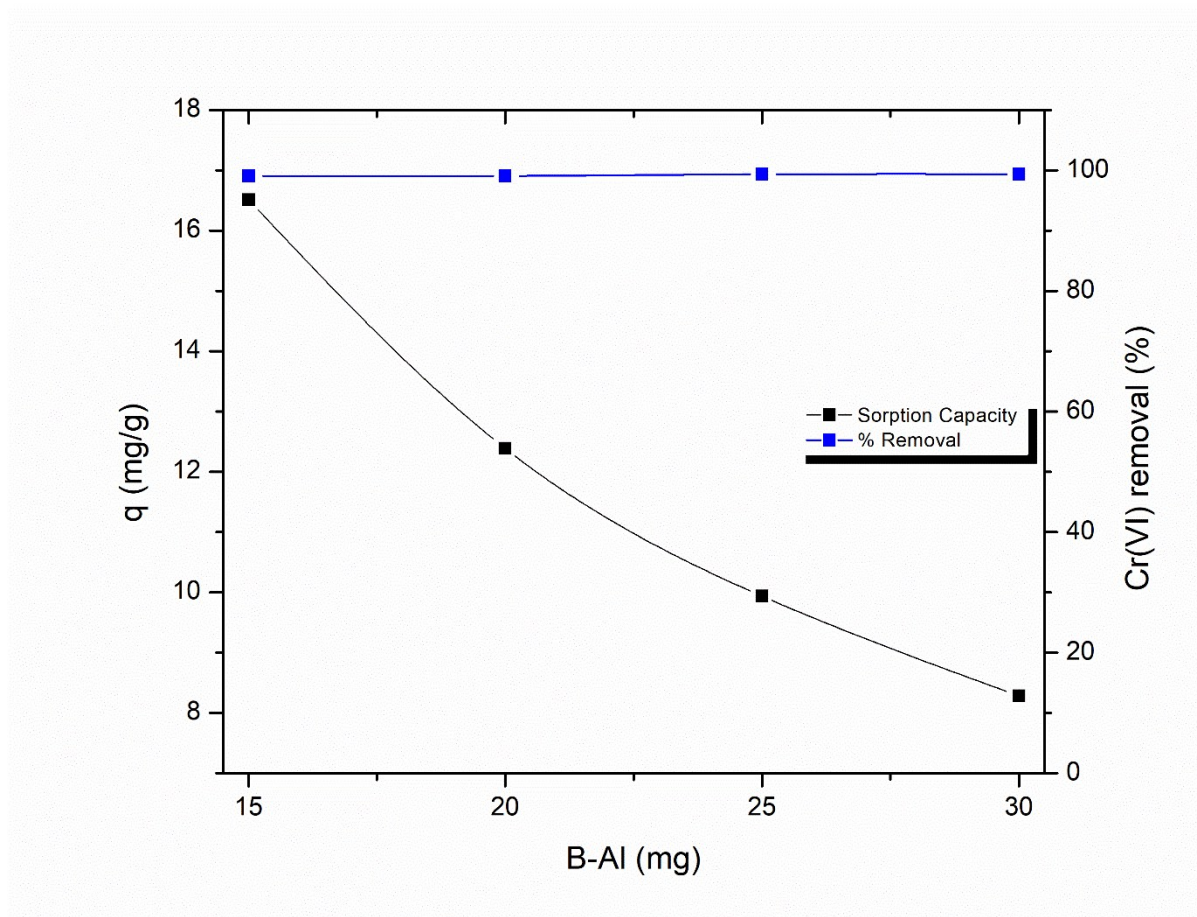


Fig. S1- Effect of solid to solution ratio on Cr(VI) removal

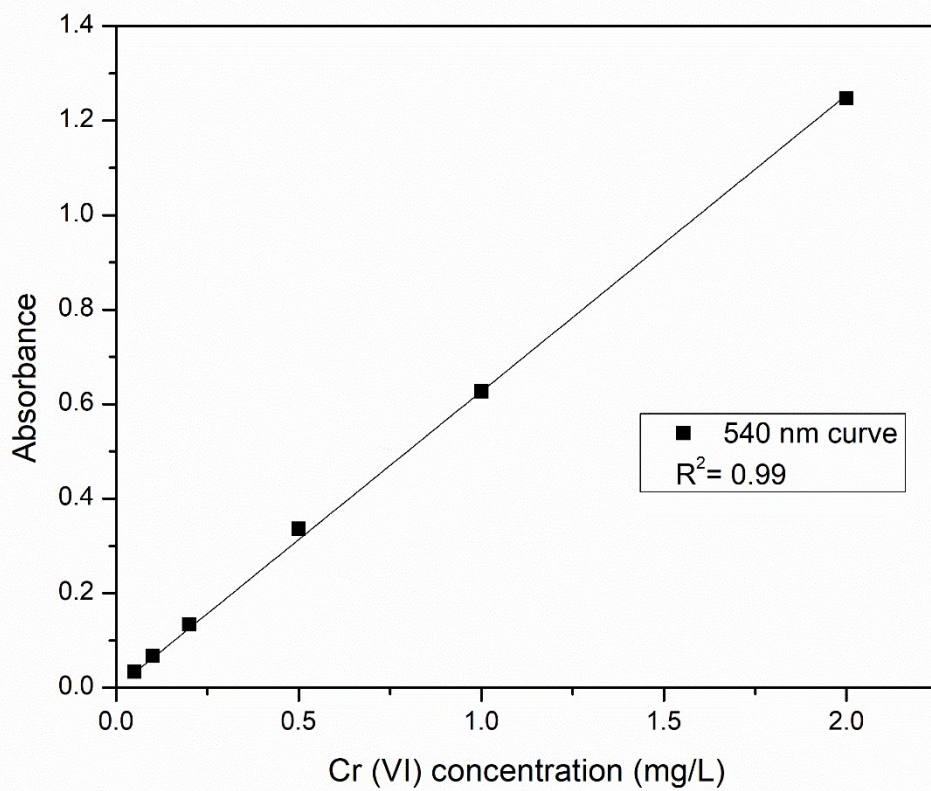
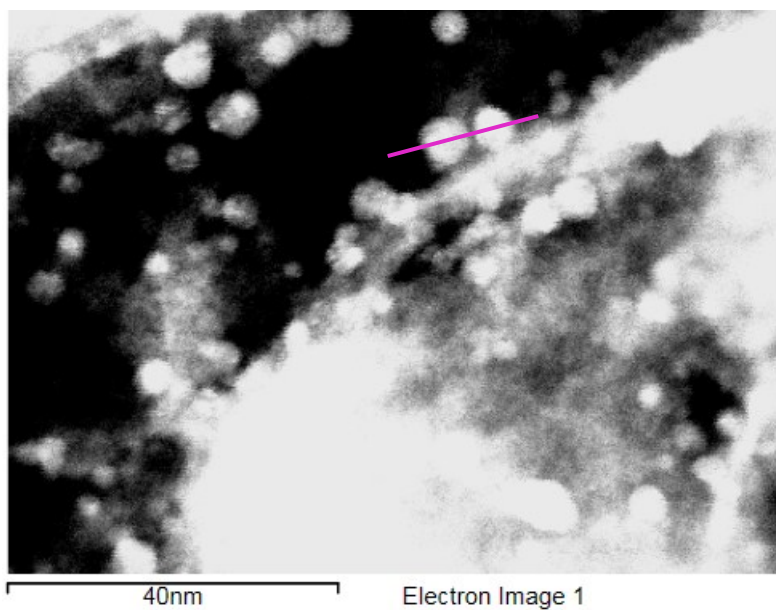


Fig. S2- Calibration curve used to determine Cr(VI) concentration using UV-Vis spectrophotometer using 1,5- diphenylcarbazide complexing agent.



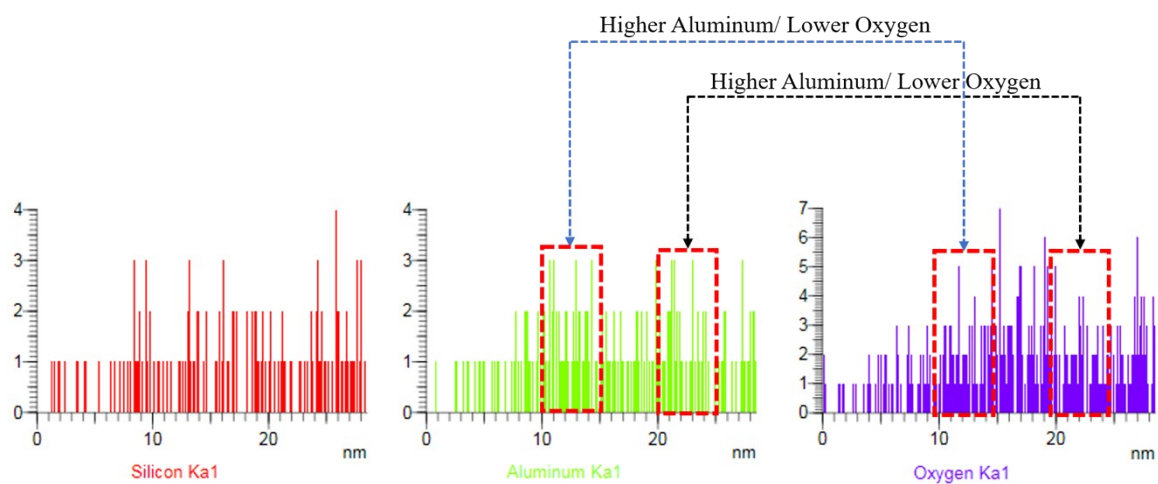


Fig. S3- STEM line scan data for Silicon, Aluminum and Oxygen

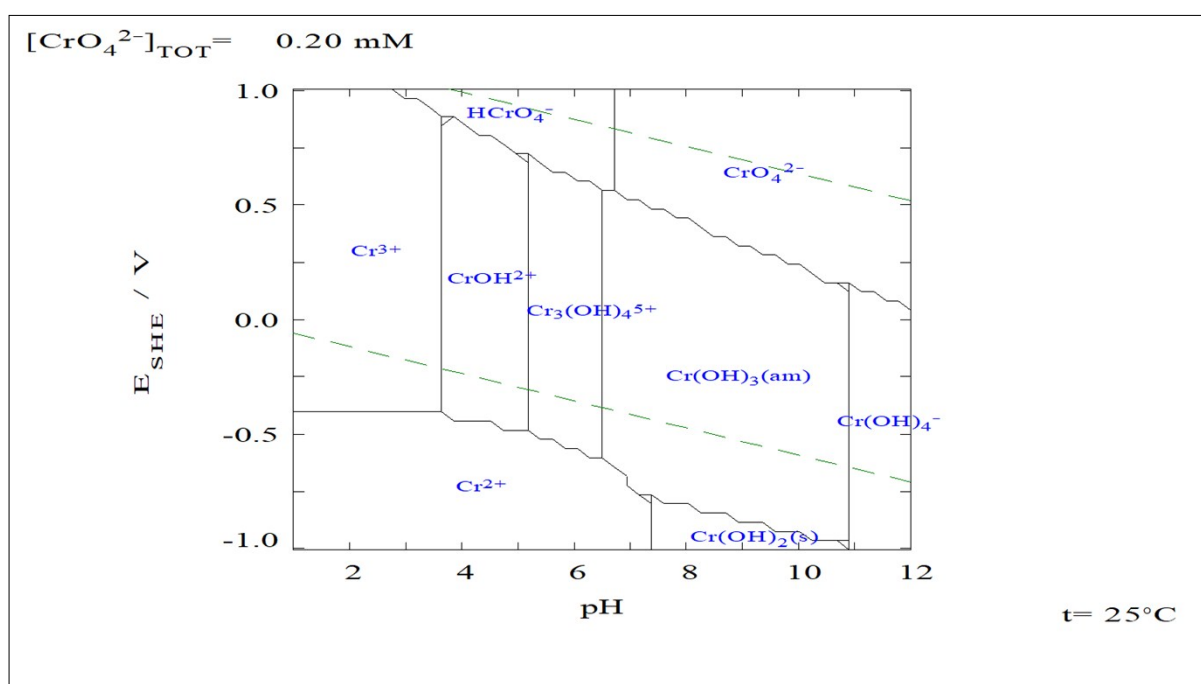


Fig. S4- Chromium speciation diagram in aqueous solutions showing HCrO_4^- and CrO_4^{2-} as relevant environmental species (Hydra-Medusa)

Adsorption Isotherms

To evaluate the interactions between sorbate and sorbent at equilibrium and to get the maximum sorption capacity, isotherm is generally used. There are two most widely used isotherms i.e. Langmuir and Freundlich adsorption isotherms. Langmuir represents the

monolayer sorption with equilibrium distribution of metal ions between the solid and liquid phases. The basic principle of Langmuir isotherm is that every adsorption site is identical and energetically equivalent [1, 2]. On the other hand, Freundlich assumes heterogeneous adsorbent surface. It represents an initial surface adsorption followed by a condensation effect resulting from strong adsorbate-adsorbate interaction [2, 3]. The linearized equations are as follows-

Langmuir adsorption isotherm

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

Freundlich adsorption isotherm

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

where C_e (mg/L) is the equilibrium concentration, q_e (mg/g) is the sorption capacity equilibrium, q_m (mg/g) and K_L (L/mg) are Langmuir constants related to maximum sorption capacity and energy of adsorption, respectively. K_F (mg/g)(L/mg)^{1/n} is the Freundlich adsorption constant and 1/n is a measure of the adsorption intensity.

Temkin adsorption isotherm

Temkin isotherm model assumes that the heat of sorption of solute in a layer decreases linearly with the blocking of the surface due to sorbent-solute interactions where sorption is characterized by uniform binding energy distribution [2]. The linearized form of Temkin isotherm is as follows-

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$$

where b (kJ/mol) is a constant related to heat of sorption, K_T (L/g) is the Temkin isotherm constant, R (0.00813 kJ/mol-K) is the gas constant, and T (K) is temperature.

DKR adsorption isotherm

In other reported isotherms, DKR isotherm is used to determine apparent energy of adsorption.

This equation works where adsorption process follows a pore filling mechanism [4-6]. The linear form of DKR isotherm equation is as following-

$$\ln q_e = \ln X_m - \beta \varepsilon^2$$

Where ε is the Polanyi potential, which is equal to-

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right)$$

Where X_m is the maximum sorption capacity, β is the activity coefficient related to mean sorption energy, R is the gas constant (kJ/kmol- K).

The mean energy of sorption (E) can be determined using following equation-

$$E = \frac{1}{\sqrt{2\beta}}$$

Reported literature and our study

Adsorbent	Conditions	Q_{\max}	Second order rate constant, k_2 (g mg ⁻¹ h ⁻¹)	Reference
B-Al nanocomposite	pH= 6.4 T= 25 °C C ₀ = 10 mg/L m/V= 0.6 g/L	49.5 mg/g	6.12	This work
Magnetic magnetite (Fe ₃ O ₄)	pH= 2 T= 25 °C C ₀ = 25 mg/L m/V= 1 g/L	20.16 mg/g	0.17	[7]
Organoclay	pH= 5 T= 23 °C C ₀ = 50 mg/L	14.64 mg/g	0.166	[8]

	m/V= 5 g/L			
Aluminum magnesium mixed hydroxide	pH= 4 T= 30 °C C ₀ = 100 mg/L m/V= 2 g/L	109.6 mg/g	1.41	[9]
layered double hydroxides on γ -Al ₂ O ₃	C ₀ = 100 mg/L m/V= 2 g/L	20.04 mg/g	0.0924	[10]
Titanium oxide-Ag composite	C ₀ = 40 mg/L pH= 2 T= 25 °C m/V= 2 g/L	25.7 mg/g	0.051	[11]

1. Boparai, H.K., M. Joseph, and D.M. O'Carroll, *Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles*. Journal of Hazardous Materials, 2011. **186**(1): p. 458-465.
2. Ayawei, N., A.N. Ebelegi, and D. Wankasi, *Modelling and Interpretation of Adsorption Isotherms*. Journal of Chemistry, 2017.
3. Choudhary, B. and D. Paul, *Isotherms, kinetics and thermodynamics of hexavalent chromium removal using biochar*. Journal of Environmental Chemical Engineering, 2018. **6**(2): p. 2335-2343.
4. Balarak, D., et al., *Langmuir, Freundlich, Temkin and Dubinin-radushkevich Isotherms Studies of Equilibrium Sorption of Ampicilin unto Montmorillonite Nanoparticles*. British Journal of Pharmaceutical Research, 2017. **20**(2).
5. A.O. Dada, A.P.O., A.M. Olatunya, O.D.A.D.A. Langmuir, *Freundlich Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn²⁺ unto phosphoric acid modified rice husk*. IOSR J. Appl. Chem., 2012. **3**(1): p. 38-45.
6. Hameed, B.H. and M.I. El-Khaiary, *Malachite green adsorption by rattan sawdust: Isotherm, kinetic and mechanism modeling*. Journal of Hazardous Materials, 2008. **159**(2-3): p. 574-579.
7. Rajput, S., C.U. Pittman, Jr., and D. Mohan, *Magnetic magnetite (Fe₃O₄) nanoparticle synthesis and applications for lead (Pb²⁺) and chromium (Cr⁶⁺) removal from water*. J Colloid Interface Sci, 2016. **468**: p. 334-346.
8. Sarkar, B., et al., *Remediation of hexavalent chromium through adsorption by bentonite based Arquad(R) 2HT-75 organoclays*. J Hazard Mater, 2010. **183**(1-3): p. 87-97.
9. Li, Y., et al., *Hexavalent chromium removal from aqueous solution by adsorption on aluminum magnesium mixed hydroxide*. Water Res, 2009. **43**(12): p. 3067-75.
10. Li, S., et al., *In situ synthesis of layered double hydroxides on gamma-Al₂O₃ and its application in chromium(VI) removal*. Water Sci Technol, 2017. **75**(5-6): p. 1466-1473.
11. Liu, S.S., et al., *Enhanced removal of trace Cr(VI) ions from aqueous solution by titanium oxide–Ag composite adsorbents*. Journal of Hazardous Materials, 2011. **190**(1): p. 723-728.