## Supporting information

## <u>Synthesis of pure nickel(III) oxide nanoparticles at room</u> <u>temperature for Cr(VI) ion removal</u>

Sayan Dey<sup>(a)</sup>, Swarupananda Bhattacharjee<sup>(a)</sup>, Mahua Ghosh Chaudhuri<sup>(a)</sup>, Raj Shekhar Bose<sup>(b)</sup>, Suman Halder<sup>(c)</sup> and Chandan Kr. Ghosh<sup>(a)</sup>

<sup>(a)</sup>School of Materials Science and Nanotechnology, Jadavpur University, Kolkata-700032, India

<sup>(b)</sup>School of Environmental Studies, Jadavpur University, Kolkata – 700032, India.

<sup>(c)</sup>Department of Pharmaceutical Technology, Jadavpur University, Kolkata – 700032, India

\* Corresponding author's e-mail ID: chandu\_ju@yahoo.co.in



Figure S -1: EDAX micrograph showing elemental composition of pure Ni<sub>2</sub>O<sub>3</sub> nanoparticles



Figure S - 2: Variation of adsorption (pH = 6,  $Ni_2O_3$  0.02 gm, speed 600 rpm) with respect to time for 2 ml stock solution (black bar) and 100 ml stock solution (red bar). Numeric represents the difference in adsorption percentage.

In order to examine human error introduced during preparation of stock solution, adsorptions were carried out using two different stock solutions (20 ml and 100 ml) keeping the concentrations fixed (0.02 gm per ml, similar to 0.4 gm in 20 ml, shown in Figure S - 2). Here we have measured the adsorption using Ni<sub>2</sub>O<sub>3</sub> nanoparticles synthesized at room temperature (RT, 25°C). The maximum difference is found to be 0.19% in the case of 3 hours of stirring time.



Figure S - 3: Variation of adsorption with respect to pH of the solution (0.4gm K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in 20 ml, 0.02 gm Ni<sub>2</sub>O<sub>3</sub>, pH = 6, time 1.5 hours, 600 rpm).

The pH value of the solution significantly affects the forms of Cr(VI) and ionic state of the Ni<sub>2</sub>O<sub>3</sub>. In this present work, the effect pH on Cr(VI) adsorption has been investigated over a wide range of pH ranging from 3 to 12. In the acidic pH (< 3), Ni<sub>2</sub>O<sub>3</sub> is found to be not stable; hence adsorption of the synthesized nanoparticles has been presented in the pH range 6 to 12 in Figure S -3. From figure it may be concluded that the adsorption is maximum at pH = 6. Interestingly, adsorption is found to be decreased for all particles in the pH range between 6 and 7. At higher pH (> 7), adsorption is noticed to be increased for nanoparticles having higher size (synthesized at 50°C and 75°C), whereas it remains almost unchanged for others two nanoparticles having smaller size (synthesized at freezing temperature and 25°C). The initial reduction of the adsorption (below pH = 7) may be attributed to the predominant electrostatic repulsion between negatively charged Ni<sub>2</sub>O<sub>3</sub> surface and negatively charged OH of surrounded Cr(VI). The higher sized particles have less surface charge (as it is examined by zeta potential measurement), so their repulsion gets reduced, as a result their Cr(VI) adsorption capability is found to be enhanced compare to lower sized particles.



Figure S - 4: Variation of Cr(VI) adsorption with respect to adsorbent dose (0.4gm K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in 20 ml, pH = 6, 1.5 hrs, 600 rpm).

The effect of adsorbent dose on Cr(VI) removal process was examined at room temperature for four different sized  $Ni_2O_3$  nanoparticles and the variation is presented in Figure S - 4. It has been clearly observed from figure that Cr(VI) removal efficiency decreases with increasing adsorbent dose and it found to be maximum at 0.02 gm of Cr(VI). Similar type of variation was observed by Chen et al.<sup>1</sup> As we increase adsorbent dose, some agglomeration of the nanoparticles is observed. Hence the lowering of the removal capacity may be attributed to the deposited agglomerated nanoparticles. We set the adsorbent dose 0.02 gm in 20 ml for all other measurement.



Figure S - 5: Adsorbate variation (pH 6, Ni<sub>2</sub>O<sub>3</sub>0.02 gm in 20 ml, 600 rpm, time 1.5 hours).

Initial concentration of Cr(VI) was varied after taking different amount of  $K_2Cr_2O_7$  viz. 0.2, 0.4, 0.6 and 0.8 gm in 20 ml of solution (shown in Figure S - 5). During this measurement, pH and amount of Ni<sub>2</sub>O<sub>3</sub> were kept fixed 6.0 and 0.40 gm respectively. It is observed from figure that the maximum adsorption takes place corresponding to 0.40 gm of  $K_2Cr_2O_7$  in 20ml water. Hence, we have chosen this concentration of  $K_2Cr_2O_7$  for all other measurements.



Figure S- 6: Variation of Cr(VI) adsorption with speed of the shaker.

Figure S –6: represents the variation of Cr(VI) removal capacity as a function shaker speed. During this experiment, we kept pH = 6, the amount of Ni<sub>2</sub>O<sub>3</sub> was taken 0.02 gm. From the figure, it may be concluded that adsorption is maximum at 600 rpm. So we set this shaking speed for all other measurements.

We have compared Cr(VI) capacity of our synthesized sample with adsorption capacity of some other materials (shown in Table T – 1 in ESI). It is interesting to note that our synthesized Ni<sub>2</sub>O<sub>3</sub> nanoparticles possess higher adsorption capacity compare to carbon coated magnetic nanoparticles,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> etc., but has less adsorption capacity than activated carbon, aluminium – magnesium mixed hydroxide. It is worthy to state that the mechanism involved Cr(VI) in the case of aluminium – magnesium mixed hydroxide is the ion exchange, not the adsorption process. Therefore fundamentally it involves different mechanism. Activated carbon though relies on adsorption possesses higher adsorption capability due to their light mass. Therefore, we may conclude that our synthesized nanoparticles have higher removal capacity of Cr(VI).

Material used	Adsorption (mg/g)	Reference
Carbon coated magnetic nanoparticles	1.52	2
Agriculture waste biomass	0.28 - 0.82	3
Graphene nanocomposites	1.03	4
Commercial α-Fe2O3	0.68	5
Commercial CeO <sub>2</sub>	0.37	6
3D flower-like CeO <sub>2</sub>	5.9	6
Aluminium – magnesium mixed hydroxide	105	7
Activated carbon	112	8
Polyaniline coated carbon fiber	18.1	9
Ni <sub>2</sub> O <sub>3</sub> nanoparticles	20.408	Present work

Table T – 1: Comparison of adsorption process with other materials

In recent time, some new materials like rosin-based biochar -  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposites<sup>10</sup>, zinc – biochar nanocomposites<sup>11</sup>, magnetic mesoporous carbon – polyaniline composites<sup>12</sup>, tartaric acid modified Pleurotus ostreatus<sup>13</sup> have been developed by researchers and they are found to have much higher Cr(VI) adsorption capacity. Importantly, their maximum adsorptions are found to be in the range of either basic pH (~ 9) or acidic pH (~ 2). But, here we obtained the maximum adsorption capacity of our synthesized sample very close to neutral pH (~ 6). So to remove Cr(VI) from aqueous solution having pH close neutral, our synthesized sample may be helpful.

Standard deviation of the measurements was calculated using the following relation for sample synthesized at room temperature as a function time (15, 30, 45, 60, 90, 120 and 180 minutes),

Standard deviation = 
$$\sqrt{\frac{1}{5}\sum_{i=1}^{5} (R_i - R_{av})^2}$$

Where,  $R_i$  and  $R_{av}$  represent the adsorption percentage for each measurement and the average adsorption respectively. The variation of standard deviation with respect to time is presented in Figure S - 7.

Accuracy of the used system (a) UV-Vis spectrophotometer (JASCO, V- 650) ± 0.002 Abs

(b) Digital balance ± 0.001 g (c) Measuring cylinder ± 0.2 ml



Figure S – 7: Variation of standard deviation of the percentage of adsorption with respect to time.



Figure S -8: UV spectrum of Cr (VI) adsorption by particles synthesized at 0°C.



Figure S - 9: UV spectrum of Cr (VI) adsorption by particles synthesized at room temperature (25°C).



Figure S – 10: UV spectrum of Cr (VI) adsorption by particles synthesized at 50°C.



Figure S - 11: UV spectrum of Cr (VI) adsorption by particles synthesized at 70°C.



Figure S – 12: Comparison of the Zeta potentials of Ni<sub>2</sub>O<sub>3</sub> nanoparticles of different size.

## References:

- 1. Y. Chen, H. Xu, S. Wang and L. Kang, RSC Adv. 2014, 4, 17805.
- J. Zhu, H. Gu, S.B. Rapole, Z. Luo, S. Pallavkar, N. Haldolaarachchige, T. J. Benson, T. C. Ho, J. Hopper, D. P. Young, S. Wei and Z. Guo, RSC Adv., 2012, 2, 4844–4856.
- 3. U. K. Garg, M. P. Kaur, V. K. Garg and D. Sud, J. Hazard. Mater., 2007, 140, 60-68.
- J. Zhu, S. Wei, H. Gu, S. B. Rapole, Q. Wang, Z. Luo, N. Haldolaarachchige, D. P. Young and Z. Guo, Environ. Sci. Technol., 2012, 46, 977–985.
- 5. L. S. Zhong, J. S. Hu, H. P. Liang, A. M. Cao, W. G. Song and L. J. Wan, Adv. Mater., 2006, 18, 2426–2431.
- 6. L.S. Zhong, J.-S. Hu, A.-M. Cao, Q. Liu, W.-G. Song and L.-J. Wan, Chem. Mater., 2007, 19, 1648–1655.
- 7. Y. Li, B. Gao, T. Wu, D. Sun, X. Li, B. Wang and F. Lu, Water Res., 2009, 43, 3067–3075.
- 8. A. El-Sikaily, A. E. Nemr, A. Khaled, O. Abdelwehab, J. Hazard. Mater., 2007, 148, 216–228.
- 9. B. Qiu, C. Xu, D. Sun, H. Wei, X. Zhang, J. Guo, Q. Wang, D. Rutman, Z. Guo, S. Wei, RSC Adv., 2014, 4, 29855.
- Z. H. Ruan, J. H. Wu, J. F. Huang, Z.T. Lin, Y. F. Li, Y. L. Liu, P. Y. Cao, Y. P. Fang, J. Xie, G. B. Jiang, J. Mater. Chem. A, 2015, 3, 4595.
- 11. C. Gan, Y. Liu, X. Tan, S. Wang, G. Zeng, B. Zheng, T. Li, Z. Jiang, W. Liu, RSC Adv., 2015, 5, 35107.
- 12. G. Yang, L. Tang, Y. Cai, G. Zeng, P. Guo, G. Chen, Y. Zhou, J. Tang, J. Chen, W. Xiong, RSC Adv., 2014, 4, 58362.
- 13. T. Y. Lin, D. H. Chen, RSC Adv., 2015, 5, 24009.