

1 **Electronic Supplementary Material**
2 **An integrated system for field analysis of Cd(II) and Pb(II) via**
3 **preconcentration using nano-TiO₂/cellulose paper composite and**
4 **subsequent detection with a portable X-ray fluorescence spectrometer**

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1. Effect of pH on the preconcentration of Pb(II) and Cd(II)

The effect of pH on the adsorption rate of Pb(II) and Cd(II) ($500 \mu\text{g L}^{-1}$) was shown in **Figure S1**. In the pH range of 3.0-9.0, the adsorption rates were the maximum at pH 5.0 and 8.0 for Pb(II) and Cd(II), respectively, and maintained at a high level of 95.5% for Pb(II) and 94.4% for Cd(II) at pH 8.0. In order to obtain a quantitative adsorption for the studied metals simultaneously, a pH of 8.0 was selected for use in this study.

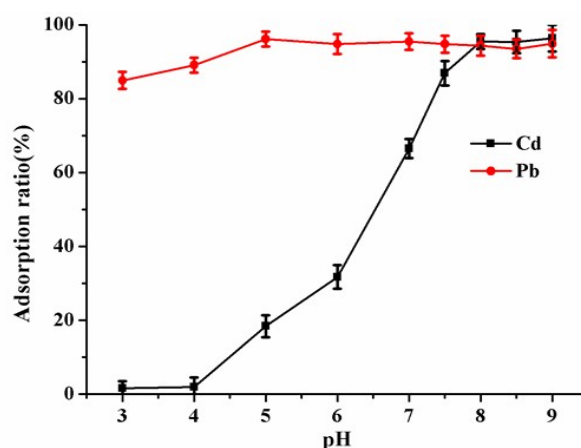


Figure S1 Effects of pH on the adsorption of Pb(II) and Cd(II) on TCP

($C_{\text{initial}} = 500 \mu\text{g L}^{-1}$, $V = 250 \text{ mL}$, $t = 3 \text{ h}$)

The mechanism of adsorption Pb(II) and Cd(II) was suggested to be the soft acid/soft base interactions to form complexes for chemisorption and electrostatic force of electric double layer model for physisorption [1]. The point of zero charge (PZC) of anatase (6 nm) was 7.2 [1]. At $\text{pH} < \text{PZC}$ and $\text{pH} > \text{PZC}$, the surface was positively and negatively charged, respectively. Generally, the physisorption was driven by electrostatic force between oppositely charged adsorbates and adsorbents. but for chemisorption, like charged ions could be interacted by chemical bond [1]. The strong pH-dependent adsorption of Cd(II) on TCP was observed, but such influence on Pb(II)

was not significant. Therefore, at $\text{pH} < 8.0$, the chemisorption ability of TCP for Pb(II) was dominant and higher than that for Cd(II) , but the adsorption of Cd(II) onto TCP was mainly due to physisorption.

2. Dynamic Adsorption of Pb(II) and Cd(II) on Nano- TiO_2 /Cellulose Paper

The dynamic adsorption of Pb(II) and Cd(II) on TCP was investigated and shown in **Figure S2**. Adsorption of Pb(II) and Cd(II) showed an increasing trend up to a reaction time of 3 h beyond which adsorption appeared to have approached equilibrium.. At $\text{pH} 8.0$, the r of Pb(II) and Cd(II) adsorption on TCP were all larger than 0.99. So, the second-order equation was suitable for heavy metals adsorption on TCP, which inferred that the chemisorption controlled the adsorption rate. The adsorption ratio of Pb(II) and Cd(II) was increased with the increasing of the adsorption time until reaching the adsorption equilibrium time (3 h), so the adsorption time of 3 h was selected for use in this study.

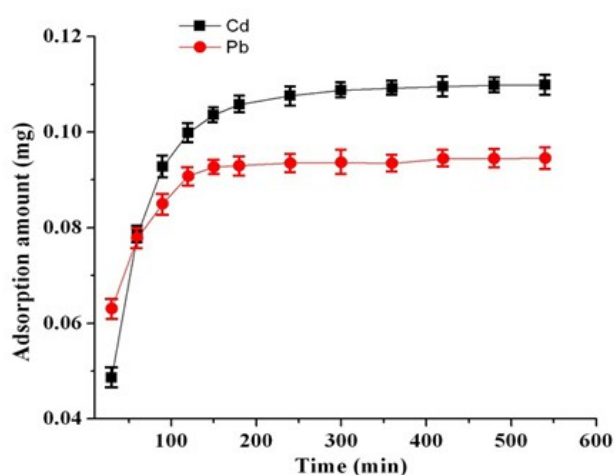


Figure S2 Dynamic adsorption of Pb(II) and Cd(II) on TCP with different time intervals

($C_{\text{initial}} = 500 \mu\text{g L}^{-1}$, $V = 250 \text{ mL}$, $\text{pH} = 8.0$)

3. Effect of volumes of samples on the preconcentration of Pb(II) and Cd(II)

The volume of samples needed for preconcentration was discussed in **Figure 3S**. The the absorption ratio of Pb(II) and Cd(II) were increased with the sample volume change from 100 mL to 1000 mL, and then kept balance at 1000 mL. Hence, 1000mL of sample volume was selected as the optimum volume for preconcentration. To trade off the enrichment factor , a sample volume of 1000 mL and an eluent volume of 0 mL were used, so that an enrichment factor of 10^3 were obtained in this work.

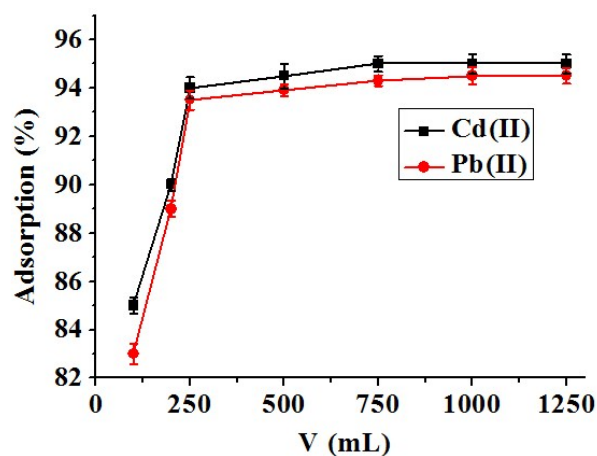


Figure S3 Effect of volumes of samples on the preconcentration of Pb(II) and Cd(II)

Table S1 Kinetic parameters for the adsorption of Pb(II) and Cd(II) on TCP at 25°C

pseudo-second-order	Q_e (mg)	k_2^K (mg min ⁻¹) ^T	r
Pb	0.0968	0.934	0.999
Cd	0.116	0.348	0.998

References

1. Xie X, Gao L (2009) Effect of crystal structure on adsorption behaviors of nanosized TiO₂ for heavy-metal cations. *Curr Appl Phys* 9: S185-S188