# Adsorption Kinetics of Pb(II), Cd(II), Zn(II) and Fe(III) onto Saponified Apple Waste

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#### Abstract

Saponified apple waste gel was prepared in wet condition with calcium hydroxide at highly alkaline medium. The effect of initial concentration, contact time and pH of the solution was investigated. The maximum adsorption capacity onto this adsorbent was investigated for Fe(III), Cd(II), Zn(II) and Pb(II) at their optimal pH of 3, 6, 4.5 and 3.5 respectively. Langmuir isotherm and pseudo second-order kinetic model gave better explanation of the adsorption process. For binary mixture of Zn(II) and Cd(II), the separation factor and effect on adsorption capacity for both the metals were investigated.

Keywords: adsorption, saponified apple waste, bioadsorption.

# Introduction

Heavy metals such as Pb(II), Fe(III), Ni(II), Zn(II), Cd(II), Cr(VI), Cu(II) are toxic pollutants released into the environment due to the different industrial, mining and agricultural activities. These heavy metals are non biodegradable and accumulated in living organism from drinking water sources. The precipitation, electrolytic recovery, chelation and solvent extraction are some examples used for the removal of these metals in the past. However, these methods are restricted due to economical and technical difficulties. Many efforts have been made to find cheaper pollution control method and materials where biosorption has emerged as an alternative cost effective technology for heavy metal removal.<sup>1-5</sup>

In present study, an attempt is made to investigate the use of apple waste as a low cost adsorbent for the removal of toxic heavy metal from aqueous solution. The aim of the study is to investigate the kinetics and mechanisms of Fe(III), Cd(II), Zn(II) and Pb(II) ion adsorption on SAW gel. The pseudo first-order, pseudo second-

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order and second order models are used to study the kinetics.

## **Experimental Methods**

100 g of wet apple waste was treated with 0.2 M of calcium hydroxide and equilibrated for 24 h using a mechanical shaker. The mixture was washed until neutral pH and then, dried at 70°C. The material prepared in this way was abbreviated as saponified apple waste (SAW) as shown in Fig. 1.



Figure 1: Modification of apple waste.

30 mL of 0.01 M sodium hydroxide solution and 20 mg of  $H^+$ – form gel were shaken for 24 h. The decrease in sodium hydroxide concentration is equal to total amount of proton in  $H^+$ – form gel and then, total exchangeable proton was evaluated.

20 mg of dried gel and 20 ml metal ion solution were agitated in a mechanical shaker for 24 h for the adsorption of metals. The concentration the metal was 10-500 mg/L. The concentrations before and after adsorption study were measured by atomic adsorption spectrometer (AAS). The optimal pH of the adsorption was also performed. 20 mL of metal ion solution of known concentration was added to 20 mg of adsorbent and mixture was stirred for 24 h for adsorption, and then analyzed for metal ions concentration by AAS. For kinetic study, 10 mg of SAW and 40 mL of metal ion solution of metals were taken and stirred for 10 minute to 24 h, and then concentration of metal ion was analyzed.

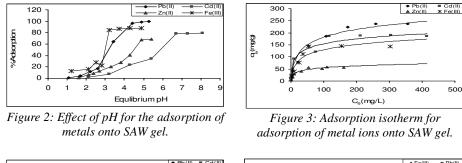
## **Results and Discussion**

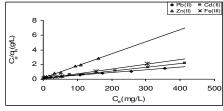
The total exchangeable cation was found to be 2.65 mol/kg, which was comparable to the maximum exchangeable cation of same analogues.

Figure 2 shows that pH of the solution highly affect the adsorption capacity. The adsorption of Fe(III), Cd(II), Zn(II) and Pb(II) onto SAW shows that adsorption capacity increases with increasing the pH of the solution. This is mostly due to the competition of H<sup>+</sup>- ion adsorption along with metal ions at low pH. Another reason for increasing metal sorption with increasing pH is due to the decrease of the solubility of these metal ions with increasing pH.<sup>6</sup> It is found that the adsorption of Fe(III), Cd(II), Zn(II) and Pb(II) is found to be maximum at pH 3, 6, 4.5 and 3.5, respectively.

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Adsorption of Fe(III), Cd(II), Zn(II) and Pb(II) onto SAW gel gives the linear relationship with Langmuir and Freundlich isotherms which is shown in Figs 3-5. A comparatively high value of correlation coefficient for Langmuir adsorption isotherm as compared to Freundlich adsorption isotherm indicated that the adsorption process was more closely fitted to the Langmuir isotherms.





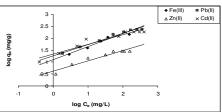


Figure 4:Langmuir plot for the adsorption of metal ions onto SAW gel.

Figure 5: Freundlich isotherm for adsorption of metal ions onto SAW gel.

Kinetic studies for the adsorption of Fe(III), Cd(II), Zn(II) and Pb(II) on SAW gel were studied using pseudo-first order, pseudo second order and second order kinetic models which are shown in Figs 6-8. Pseudo second order kinetic plot of  $(t/q_t)$  (min. g/mg) versus t (min) gave the perfect straight line for the adsorption of all metal ions onto SAW gel indicating that adsorption reaction can be approximated with pseudo-second order kinetic model.<sup>4-6</sup> Furthermore, the adsorption capacity of the material evaluated experimentally seems to be quite high as compared to the materials mentioned in the literature.<sup>6</sup> High value of correlation coefficient in pseudo-second order plot for all the metals than pseudo-first order and second order plot are additional evidence to confirm that the adsorption reaction proceeded by the pseudo second order kinetic model.

Figure 9 shows the selectivity of Cd(II) over Zn(II) in terms of separation factor which is found to be maximum i.e. 26.6 at pH 7 indicating that, they can be separated easily from the mixture. Adsorption capacity of Cd(II) and Zn(II) in single metal system were reported previously to be 12.37 and 8.62 mg/g, while it was reduced to 12.12 and 6.62 mg/g, respectively, when determined from the binary mixture solution. This shows that presence of other metal ions in the solution suppressed the adsorption capacity of metal ion onto the SAW.

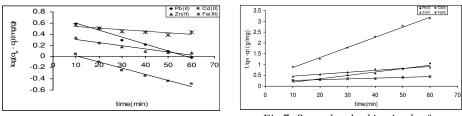


Figure 6: Pseudo first order plot for adsorption of metals onto SAW gel.

*Fig 7: Second order kinetic plot for adsorption of some metal ions onto SAW gel.* 

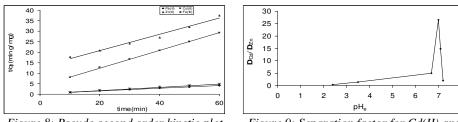


Figure 8: Pseudo second order kinetic plot for some metal ions onto SAW gel

Figure 9: Separation factor for Cd(II) and Zn(II) onto SAW gel.

## Conclusions

Apple waste was converted into low cost and effective adsorbent by saponification. Maximum exchangeable cation was evaluated to be 2.65 mole/Kg. The maximum adsorption capacity of Fe(III), Cd(II), Zn(II) and Pb(II) is investigated to be 144.9, 196, 62.5 and 256.4 mg/g at their optimal pH 3, 6, 4.5 and 3.5, respectively. Langmuir isotherm and pseudo second-order kinetic model gave best description of the adsorption process. Separation factor of Cd(II) over Zn(II) in binary mixture was found to be 26.6 at pH 7.

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