COMPETITIVE ADSORPTION OF LEAD AND CHROMIUM ONTO SAWDUST

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Abstract: The equilibrium and kinetics of adsorption of Cr(VI) and Pb(II) ions from the binary solution onto sawdust was investigated. The batch adsorption techniques were employed in the studies. The effect of pH, contact time and initial concentration were investigated. The optimum pH for adsorption of Cr(VI) and Pb(II) ion were 4 and 5 respectively. The experimental data best fit to the Langmui rwith a correlation coefficient of 1. The adsorption capacity of the sawdust for Cr(VI) and Pb(II) ions were 0.92 and 0.89 mgg^{-1} respectively. The energy of adsorption obtained from the Dubinin Raduskevich model shows that chemisorption was dominant. The adsorption process follows a pseudo second order model, with a correlation coefficient of 1 for both metal ions.

Keywords: Langmuir isotherm, chemisorption, sawdust, heavymetals

Introduction

Excessive release of lead and chromium into the environment due to industrialisation and urbanisation has posed a great problem worldwide. Unlike organic pollutants, majority of which are susceptible to biological degradation, heavy metals ions do not degrade into harmless end products. The presence of these heavy metals ions is a major concern due to their toxicity to life forms. Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, and tanneries, and smelting industries (Kadirvelu *et al.*, 2000). The metals exist in the waste water in the form of multi element wastewater. The removal of Pb and Cr from waste water has been achieved by various techniques including precipitation, membrane filtration, ion exchange, co-precipitation and adsorption. Studies have shown that the technique of adsorption remains the most and effectiveness and most economical.

Several reports on adsorption capacities of carbon materials and biomass are found in literatures. However, information on the effects of the presence of other ions on adsorption effectiveness and capacity from wastewater are scanty. The adsorption mechanism of ion from a binary or multi ion wastewater is also ambiguous. This work therefore sought to investigate adsorption of Pb and Cr from the binary solution. The factors that could influence the adsorption of either of the heavy metal from the solution and the mechanism of the adsorption process are also investigated.

Materials and Methods

Materials

Analytical grade lead nitrate and potassium dichromate manufactured by British Drug House (BDH) Chemicals England were obtained and used for the preparation of adsorbate solution. Deionize distilled water was used for all preparation. Alpha 4 Atomic Adsorption spectrophotometer was used for the determination of the metals concentrations.

Methods

Sawdust was collected from a local saw mill in Samaru-Zaria, Kaduna state. The sawdust was washed with deionised water until water eluted was relatively clear. The saw dust was oven dried at a temperature of 100^{o}C for 24 h (Bulut and Tez, 2007; Erwaand Ibrahim, 2016). The saw dust was crushed and sieved to 625 µm particle size. This was used directly without any pre-treatment as adsorbent for the removal of the metals from aqueous solution.

Effect of contact time on adsorption of the metals from solution

The competitive sorption experiments were carried out using the method described by Koffi *et al.* (2010). For each experiment, 25 cm^3 of both lead nitrate solution and potassium dichromate solution of known concentrations (20 ppm) were measured into a 150 cm^3 conical flask. 1 gram of sawdust was weighed and transferred into the conical flasks with an air tight stopper. This mixture was agitated using a rotatory shaker at room temperature and at a constant speed. The flasks were agitated for a time interval of 30, 60, 90, 120 and 150 min.

Effect of initial concentration on adsorption of the metals from solution

The equilibrium studies were carried out by agitating 25 cm^3 of 20 ppm lead nitrate in 1 g sawdust in presence of varying concentration of potassium dichromate (5-20 ppm) for 60 min. The experiment was repeated with 25 cm^3 of 20 ppm potassium dichromate in 1 g adsorbent in presence of varying concentration of lead nitrate solution (5-20 ppm) for a contact time of 60 min. Adsorption studies were also carried out at pH between 4 and 8, by agitating 1 g of the sawdust with a fixed concentration of both metals (20 ppm) for 60 min. The sawdust was separated from the mixture by filtration using a Whatman No. 1 filter paper after agitation and the filtrate was taken for analyses using the Alpha 4 Atomic Absorption Spectrophotometer.

Results and Discussions

Effect of contact time

Figure 1 shows that the sawdust had a preferential adsorption for the Cr(VI) with 99.28% adsorbed after 60 min. while the highest adsorption for Pb(II) was 96.67% in 90 min. It is seen that there was a rapid uptake of the metals for the first 30 min. The trend changed as contact time increased. The Pb(II) adsorption decreased at the beginning while that of Cr(VI) increased. This can be attributed, basically to the size of the metals ions. The small size of the Cr(VI) makes it easier to attach more and faster to adsorption sites on the adsorbent. Similar trend has been reported in literature (Uzun and Guzel, 2000). However, there was an average increase in the adsorption of the metals suggesting that in a binary solution, despite jostling for adsorption sites, the two metals are on average adsorbed as time increases till saturation of the adsorbent occurs. This observation differs from that reported between cation dyes and dispersed dyes where competitive adsorption increased the time of attaining equilibrium of disperse dye in presence of cationic dyes (Sun *et al*., 2013).

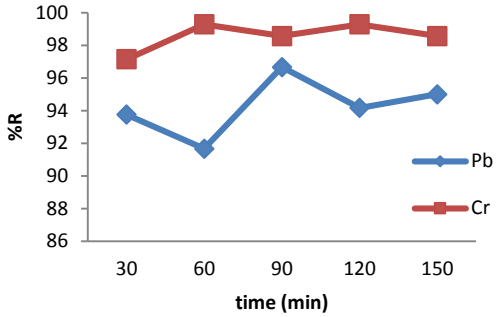

Fig. 1: Effect of contact time on adsorption of Cr(VI) and Pb(II) from a binary solution

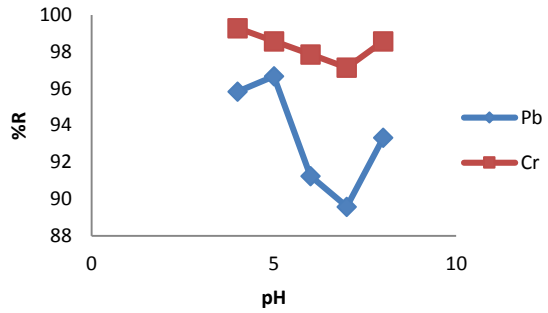

Fig. 2: Effect of pH on the adsorption of Cr and Pb from a binary mixture

Effect of pH

pH is one of the most important factor that affect the adsorption of metals. The pH dependent study of the adsorption is shown in Fig. 2. From the graph, the pH has its own contribution to the adsorption capacities. The result shows that, at pH 4, Cr(VI) adsorption was maximum (R= 99.28%). Dermirbas *et al.* (2004), reported that Cr(VI) in its dominant form $HCrO^-$, adsorbs best at pH 2 and on increasing pH (between 2 and 6), the Cr(VI) changes its form to CrO_4^- and $Cr_2O_7^-$. In basic solutions, the tetrahedral yellow chromate ion, CrO_4^- exists in the form CrO_3.

The maximum adsorption pH for chromium for this study was 4. This shows that chromium adsorption occurs better in acidic medium and the most favourable form in which Cr(VI) is adsorbed is $HCrO^-$. Similar trend was observed for the adsorption of Pb(II). There was an increase in adsorption up to pH 5. The variation in % adsorbed with pH may be adduced to the difference in the inter-particle interactions and for the fact that the adsorption may be particle diffusion controlled. Possibly, the trend was also influenced by competition between hydrogen ions, Cr ions and Pb ions. Similar results for the individual ions have been reported in literature (Kalyani *et al.*, 2010).

Effect of initial metal ion concentration

Figure 3(a) shows removal of Pb(II) at varying concentration in the presence of a constant concentration (20 ppm) of Cr(VI). The Cr(VI) adsorbed was 96% and remained relatively a constant. It was observed that there was increase in % removal of the Pb(II) as the initial concentration was increased from 5 to 25 ppm. At 5p pm, the ratio of Pb(II) concentration to Cr(VI) concentration was 1:4, hence the competition for adsorption sites favours Cr(VI) in terms of concentration of ions present at 5 ppm. As the concentration of Pb(II) increases, the competitive power for Pb(II) becomes higher which leads to increased adsorption of Pb(II). At 25 ppm, the adsorption of Pb(II) increased to 98% while the adsorption of Cr(VI) reduced a little to 95.5% because of higher concentration of Pb(II) ions. This suggests that the concentration of ions present plays an important role in the adsorption process and in some cases; outweigh the effect of ionic size and inter-particle interaction.

The trend shown in Fig. 3(b) differs from that observed in Figure 3(a). The dominating factor in this adsorption is ionic size and inter-particle interaction. It is obvious from Fig. 3 (b) that increasing the concentration of Cr(VI) ions decreases the adsorption of Pb(II) ions. At 10 ppm, the adsorption of Cr(VI) increased from 90 to 93.8% while that for Pb(II) decreased from 95.5 to 93.7%. The percentage of Cr(VI)adsorbed continues to increase even up to 97.8% while that for Pb(II) was fluctuating. This suggests that the dominating factor in this adsorption process is the ionic size.

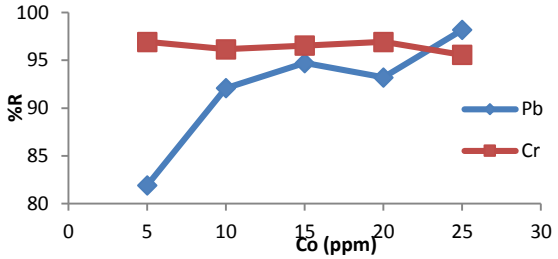

Fig. 3(a): Effect of initial concentration on adsorption of Pb(II) from binary solution (Adsorbent dose -1 g, contact time -60 min, conc. Cr(VI) -20 ppm)

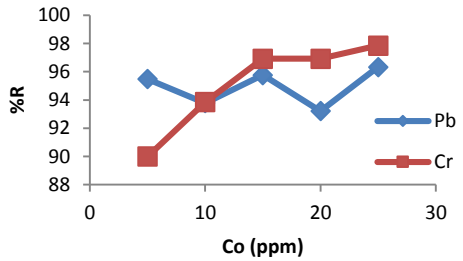

Fig. 3(b): Effect of initial concentration on adsorption of Cr(VI) from binary solution (Adsorbent dose -1 g, contact time - 60 min, conc Pb(II) -20 ppm)

Adsorption isotherms

The adsorption isotherm indicates how the adsorbed molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose (Hameed *et al.*, 2006).

Langmuir isotherm

The linear form of Langmuir's isotherm model is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \left(\frac{1}{Q_o}\right) C_e \qquad (1)$$

Where C_e is equilibrium concentration of adsorbate (ppm),q_e is the amount of adsorbate adsorbed per unit mass of adsorbate (mgg^{-1}), Q_o and b are Langmuir constants related to adsorption capacity and rate of adsorption relatively. A plot of $\frac{C_e}{q_e}$ against C_e gives a straight line with slope $\frac{1}{Q_o}$, indicating that the adsorption of the two metals follows Langmuir adsorption model as shown in Fig. 4(a) and 4(b).

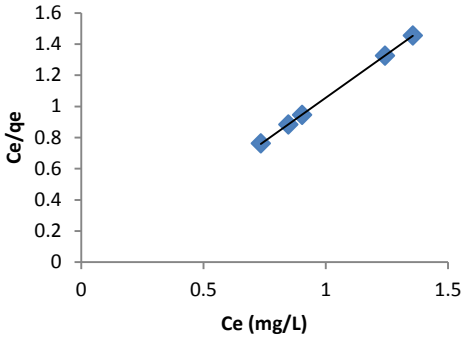

Fig. 4(a): Langmuir plot for adsorption of Cr(VI) from the binary solution

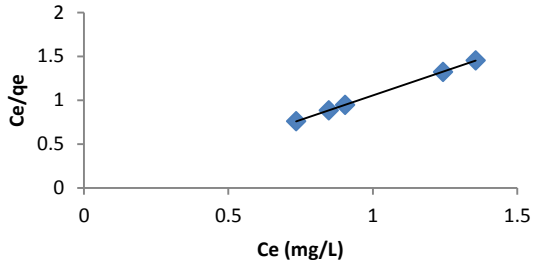

Fig. 4(b): Langmuir plot for adsorption of Pb(II) from the binary solution

The values of Q_o and b were calculated from the slopes and intercepts of the Langmuir plots. The correlation coefficients, $R^2 = 1$ for the two metal ions in the mixture shows that the adsorption fits well into the Langmuir adsorption isotherm. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter R_L which is defined by:

$$R_L = \frac{1}{1 + bC_o} \qquad (2)$$

Where C_o is the highest concentration, the value of R_L indicates the type of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($R_L < 1$) or irreversible ($R_L = 0$) (Hameed *et al.*, 2006). The R_L values for the two metal ions were found to be 0.0021 for Pb(II) and 0.0011 for Cr(VI) (Table 1) and this confirms a favourable adsorption of Cr(VI) and Pb(II) onto sawdust adsorbent.

Table 1: Isotherms Constant Parameters for the various adsorption models

Heavy metals	Langmuir			Freudlich			Dubinin Radiskevich			
	Q_o	b	R^2	R_L	1/n	K_f	R^2	E	q_D	R^2
Pb	0.89	19.20	1	$2.1x10^{-3}$	0.054	0.95	0.99	158	0.88	0.98
Cr	0.92	37.15	1	$1.1x10^{-3}$	0.038	0.95	0.99	182	0.91	0.99

Freundlich Isotherm

The well-known logarithmic form of Freundlich model is given by equation 3;

$$\log q_e = \log K_F + [\frac{1}{n}] \log C_e \qquad (3)$$

Where; q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (ppm) and K_F and n are Freundlich constants, n giving how favourable the adsorption process and K_F is the adsorption capacity of the adsorbent and it represents the quantity of metal ion adsorbed onto sawdust adsorbent for a unit equilibrium concentration.

The slope 1/n, ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero (Haghereshtet *et al.*, 1998). The 1/n values obtained for the Freundlich isotherm for both metal ions (Cr(VI) and Pb(II) (Table 1) indicates that the adsorption process follows the Freundlich isotherm. The Freundlich plot for the adsorption of Cr(VI) in the experiment is given in Figs. 5a and 5b.

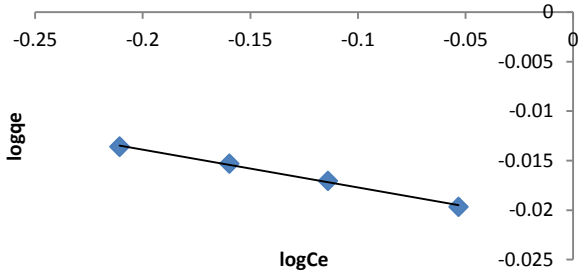

Fig.5(a). Freundlich plot for adsorption of Cr(VI)

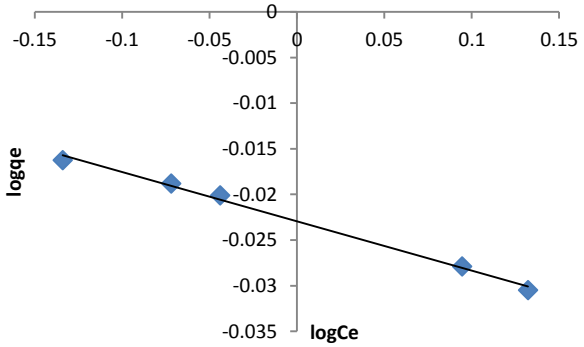

Fig. 5(b): Freundlich plot for adsorption of Pb(II)

Dubinin Raduskevich isotherm

This isotherm model was chosen to estimate the characteristics porosity of the sawdust and apparent energy of adsorption. The model is represented by the equation 4:

$$q_e = q_D \exp(-B_D [RT \ln(1 + \frac{1}{C_e})]^2) \qquad (4)$$

Where; B_D is related to the free energy of sorption per mole of the sorbate, and q_D is the Dubinin Raduskevich isotherm constant related to the degree of sorbate sorption by the sorbent surface (Horsfall *et al.*, 2005). The linear form of the equation is given as

$$L\, nq_e = l\, nq_D - 2B_D RT \ln(1 + \frac{1}{C_e}) \qquad (5)$$

A plot of l nq$_e$ against RTln(1 + $\frac{1}{C_e}$) yields straight lines and indicates good fits of the isotherm to the experimental data. The Dubinin Raduskevich plot for the adsorption of Cr(VI) in the experiment is given below (Fig. 6(a) and 6(b).

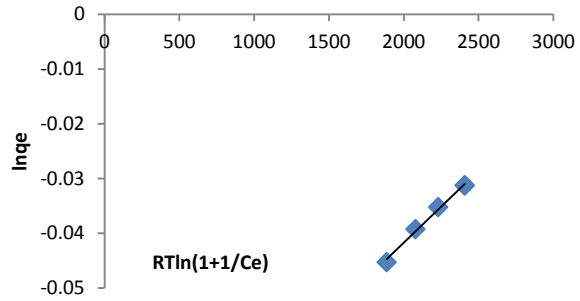

Fig.6 (a): Dubinin Raduskevich plot for adsorption of Cr(VI)

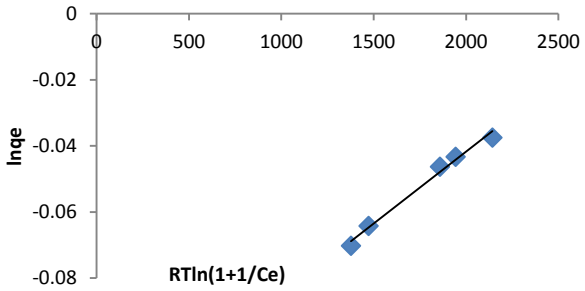

Fig. 6(b): Dubinin Raduskevich plot for adsorption of Pb(II)

The apparent energy, E of adsorption from the Dubinin Raduskevich isotherm model can be computed using the relation given below (Horsfall *et al.*, 2005).

$$E = \frac{1}{\sqrt{2B_D}} \qquad (6)$$

The Energy parameter gives information about sorption mechanism as chemical ion exchange or physical sorption. If the magnitude of E is between 200 and 400 kJ/mol, the sorption process follows chemical ion exchange, while if the magnitude of E is between 20 and 40 kJ/mol, the sorption process is of a physical nature. In the present study, the mean free energy of sorption was found to be 158 kJ/mol for Pb(II) and 182 kJ/mol for Cr(VI) (Table 1) indicating chemisorption process. The correlation coefficients R^2 for the two metal ions, 0.988 for Pb(II) and 0.994 indicates that the adsorption process fits well to the Dubinin Raduskevich model.

Kinetic studies

The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The pseudo-first and second order equations are as described by Abechi *et al.* (2011)

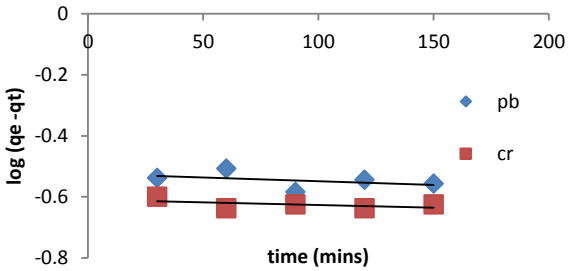

Fig. 7: Pseudo first-order kinetic Model plot

Table 2 shows a variation in the experimental amount adsorbed and the calculated amount adsorbed. This indicates that the adsorption process does not follow the pseudo first-order model. The correlation coefficients, R^2, with values of 0.18 and 0.25 (Table 2), is another evidence that the model does not describe the experimental data. The pseudo first-order rate was not calculated due to the nature of the slope of the graph which also indicates that the adsorption process does not follow the pseudo-first order model.

The fit of the experimental data to pseudo second-order kinetic model is shown in Fig. 8. The constant parameters are shown in Table 2.

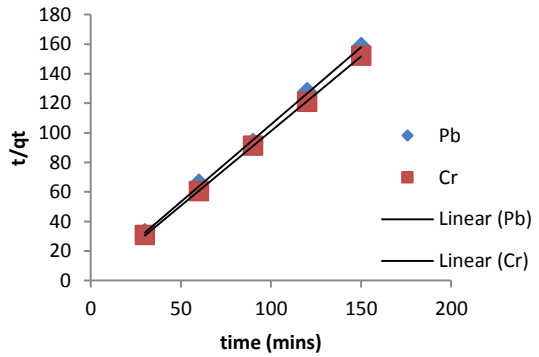

Fig. 8: Pseudo second-order kinetic model plot

Table 2: The constant parameters for the various kinetic models

Heavy metals	Pseudo first-order				Pseudo second-order				
	k_1	$q_{e(calc)}$	$q_{e(exp)}$	R^2	k_2	$q_{e(calc)}$	$q_{e(exp)}$	h	R^2
Pb	4.6x10^{-4}	0.30	1.22	0.18	1.04	0.96	0.93	0.96	0.99
Cr	4.6x10^{-4}	0.24	1.23	0.25	4.51	0.99	0.96	4.43	0.99

The pseudo-second order rate constant k_2 was found to be higher for the adsorption of Cr(VI) in the mixture than the rate of adsorption of Pb(II) indicating that the Cr(VI) is adsorbed faster than the Pb(II) in the mixture. The $q_{e(calc)}$ and $q_{e(exp)}$ values for the two metals were found to differ by ± 0.02 mgg^{-1}. This difference has also been recorded by Abechi *et al.* (2011). This shows that the adsorption follows the pseudo second-order model. The correlation coefficient of 0.999 for the two metals also indicates that the adsorption follows the second-order kinetic model.

Intraparticle diffusion kinetics model

The intraparticle diffusion model is as expressed by Abechi *et al.* (2011).

$$R = k_{id}\,(t)^a \qquad (7)$$

A linear form of the above equation is followed by the below equation;

$$\log R = \log k_{id} + a\log(t) \quad (8)$$

Where; R is the percentCr(VI) adsorbed, t is the contact time (mins), a is the gradient of linear plots, k_{id} is the intraparticle diffusion constant ($mins^{-1}$). k_{id} may be taken as a rate factor (percent of metal ion adsorbed per unit time) (Dermirbas *et al.*, 2004), and depicts the adsorption mechanism.

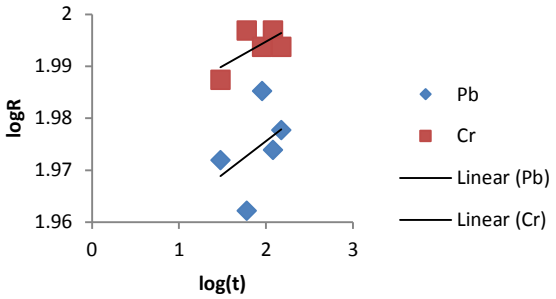

Fig. 9: The intraparticle diffusion kinetic model plot

The low correlation coefficients indicate a low contribution of the intraprticle diffusion. However, a higher correlation coefficient of 0.448 for Cr(VI) ion shows that intra-particle diffusion controls Cr(VI) adsorption more than it controls Pb(II) adsorption in the binary mixture. The k_{id} values is indicative of the rate of adsorption. The K_{id} value for adsorption of Cr(VI) ion was 94.62 while that of Pb(II) was 88.92. The larger value for Cr(VI) indicate a higher rate of adsorption compared to adsorption of Pb(II).

Conclusion

This study shows the potentiality offered by sawdust for the sorption of Cr(VI) and Pb(II) from industrial effluents. Evidence are given by this research work that the presence of Pb(II) in a solution affected the adsorption of Cr(VI) and vice versa. It has been established in this work that the relative concentration of ions present plays an important role in the preferential adsorption. This could outweigh the effect of ionic size and inter-particle interaction in competitive adsorption. The adsorption process for the metals could be best described by the Langmuir isotherms with the correlation coefficient of 1 for both metal ions. The pseudo-first order, pseudo-second order kinetic and intraparticle diffusion kinetic models were used to describe the kinetic data for Pb(II) and Cr(VI) adsorption process from the binary mixtures. It was found that the adsorption of the metals from the mixture followed the pseudo second-order kinetic model with k_2 for Pb(II) calculated as 1.04 and 4.51 for Cr(VI). The study demonstrates the suitability of sawdust for the removal of a mixture of metal ions from industrial effluents.

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