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Removal of Ni, Cd, Pb, Zn and colour from aqueous solution using potential low cost adsorbent

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A study was conducted to determine the removal efficiency of heavy metals (Ni, Cd, Pb and Zn) and colour from wastewater using cheap available materials in Malaysia such as charcoal, coconut shell carbon and a mixture of these carbons with limestone. As activated carbon is quite expensive, this study attempts to investigate the possibility of mixing activated carbon with these materials for cost saving. The suitability of using coconut shell after heating at 500°C in treating wastewater also formed the basis of the study. Batch studies were carried out in the laboratory with an initial concentration of heavy metals generally found in final effluents at 2 mg/L and colour at 400-ptCo. The results indicated that a mixture of activated carbon and limestone had removed 92% of heavy metals and 85% of colour from synthetic wastewater at a wide range of *p*H. When activated carbon was only used, 85% of heavy metals and 99% of colour were removed. For a mixture of charcoal with limestone, the removal efficiencies for heavy metals and colour were at 65% and 35%, respectively. The removal efficiency for heavy metals was further improved to 80% when charcoal was used, but for colour removal it was only 30%. The results of the study suggested that a mixture of activated carbon with limestone had significantly removed the amount of heavy metals and colour. Thus, the cost of the overall process can be reduced. This study also indicated that there is possibility of using coconut carbon and charcoal as an alternative absorbents for removing heavy metals and colour from wastewater. However, improvement on activation process is required.

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Heavy metals such as cadmium, lead, nickel, copper and chromium (III) and their compounds are being used widely in industries such as steel, electroplating, battery, paint and pigment. Because of their toxicity, the presence of any of these metals in excessive quantities will interfere with many beneficial uses of water, and may endangered aquatic life. As a result, the standard B discharge limit of these metals under Environmental Quality Act 1974 of Malaysia, (Sewage and Industrial Effluents) is kept below 1.0 mg/L with 0.02 mg/L for Cd, 0.50 mg/L for Pb, 1.0 mg/L each for Zn and Ni[1].

There are a few methods available for reducing the concentrations of heavy metals in water and wastewater. Heavy metals may be removed via precipitation with hydroxide, ion exchange, reverse osmosis, electrodialysis, oxidation and reduction and adsorption. For example, in precipitation the *p*H of wastewater has to be raised with chemical agent (generally by addition of calcium hydroxide) in order to allow metals to settle as metal hydroxides which may be removed through sedimentation and filtration. Even though the method is popular compared with others, its usage for long term is expensive in terms of chemicals used and costly operation and maintenance and generating significant amount of metallic sludge which requires proper handling and disposal. Other methods of heavy metals removal have been reported by various authors. These include cadmium desorption in sand through batch and flow-through methods[2]; removal and recovery of Ni (II), Zn (II), Cr (VI) and Cu (II) from electroplating wastewater by using Kyanite as an adsorbent[3]; removal of Pb, Cd, Ni, Cr, Cu, Ca, Mg and Mn by sequential adsorbent treatment using alumina[4].

The use of limestone as sole particle in removing heavy metals at concentration normally found in groundwater and natural waters has been studied previously[5,6]. At a final pH 8.5 (initial pH 5.5 to 9.0), 95% of Mn was removed from the solution from an initial concentration of 1 mg/L or equivalent to 0.114 μg/g. More than 80% removal of heavy metals

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(1 mg/g) such as iron, manganese and cadmium can be achieved by batch experiment or continuous flow filtration process, using limestone alone as sole media[7].

Colour in water and wastewater may be present from naturally occurring metals such as Fe^{2+}, Cr^{3+} and Mn^{2+}, humus, plankton and industrial wastes that contain pigments. Pigments are widely used in industries such as paints, ceramic, food and drinks, medicine, cosmetics and plastics. Colour in wastewater may be derived from organic and non-organic sources. Water pollution by non-organic colour containing coloured metal ions such as Cr^{3+} may cause adverse impacts on health.

Various techniques may be used to remove colour from wastewater. These include chemical precipitation, rapid sand filtration, membrane processes, ion exchange, ozonation and adsorption using activated carbon[8]. Adsorption and membrane processes are efficient but expensive[9]. Application of various adsorbents for colour removal has been reported by many researchers. These include the use of shale oil ash[10]; sorption by biosorbent waste product pitch[11]; natural adsorbents (i.e., Anodonta shell and Sepia pen.)[12]; granular activated carbons made from binders and agricultural by-products[13]; chitosan[14]; coal based sorbents[15]; coir pitch[16]; calcined alunite and granular activated carbon[17]; activated clay[18].

At present, there is a growing interest in using low cost, commercially available materials for the adsorption of dyes. A wide variety of materials such as fly ash[19,20], peat[21], phenolic resin[22], wood[23], maise cob[24], natural clays[25], activated sludge[26], wood chips[27], jift[28], palm-fruit bunch particles[29], nanosize modified silica[30], sugar beet pulp[31], activated carbon from fertilizer waste[32], olive mill products[33], activated slag[32,34], bassage fly ash[35], are being used as low cost alternatives to activated carbon.

To date, most studies of the adsorption capacities of waste materials have been concentrated on the removal of organic compounds from simple synthetic solutions. Limited work has been reported on the effectiveness of these types of adsorbents when dealing with coloured, aqueous effluents from a chemical plant[31].

Colour and heavy metals are quite commonly present together in some industrial wastewater such as pharmaceutical industry[36], paper mill effluent[37], organic chemicals wastewater[38], and semi-aerobic landfill leachate[39]. Both parameters are also included as leachate sampling parameter[40]. Therefore, the objective of the study is to determine the suitability of using different adsorbents in removing color and heavy metals (Ni, Cd, Pb, and Zn) from aqueous solutions. The adsorbents investigated included activated carbon, charcoal, coconut shell carbon, limestone and some combinations between adsorbents. The efficiency of limestone for removing heavy metals was examined in the batch experiments and the results were compared with experiments using activated carbon. As activated carbon is quite costly, the study also aims to investigate possibility of mixing these cheap materials (charcoal and coconut shell carbon) with limestone, which is cheap in cost. The limestone used in the experiment was considered fairly low cost as the price ranges from Rs. 100 to Rs. 400 per metric ton as compared to the cost of activated carbon which is Rs. 20-90 per kg. Coconut shell carbon is a waste material and charcoal costs around Rs. 4 per kg.

Materials and Methods

Properties of adsorbents

Coconut shell carbon was manually prepared in the laboratory from coconut shell. The shell was burnt in muffle furnace at a temperature of 500°C for 4-5 min. The carbon was then left to cool in an oven at a temperature of 105°C for 24 h. The material was not subjected to any further pretreatment before use. Prior to the experiment, the composition of limestone was determined via digestion method with strong concentrated acid followed by metal determinations by an Atomic Absorption Spectrophotometer (AAS). Limestone, charcoal and coconut shell carbons were sieved to obtain a size between 2.36 mm and 4.75 mm. Adsorbent's density was determined by a conventional method, i.e., weight/volume of adsorbent. Properties of adsorbent used in the studies are shown in Table 1.

Shaking experiments

Coconut shell carbon of 45 g weight (equivalent to 100 g limestone by volume) was put into 350 mL conical flask that contains 120 mL of a mixture of heavy metal solution (copper, nickel, zinc, lead, cadmium and chromium) with an initial concentration of 2 mg/L, which equals to 0.24 mg metals. Heavy metal solutions were prepared from AnalaR grade standard solution. Food colour containing a mixture of 4% Tartrazine (C.I. 19140), Brilliant Blue FCF (C.I. 42090) and Carmoisine (C.I. 14720) at a concentration of 400 PtCo was then added to the flask. Blank test was undertaken beforehand in order to ensure the pigments do not contain heavy metals. pH of sample was adjusted to desired value using solutions of hydrochloric acid (HCl) and sodium hydroxide (NaOH). A total of 9 flasks were used at different pH values of 3, 4, 5, 6, 7, 8, 9, and 10 and recorded as initial pH. The flasks were shaken by an orbital shaker at 300 rpm for 60 min as stated elsewhere. After shaking for 60 min, the pH of samples was measured and recorded as final pH. The solution was left to settle for 90 min. The supernatant was analysed for metals and colour. An AAS (Model Shimadzu A660) with reading up to ±0.01 mg/L was used for metals determination as detailed elsewhere[41]. The instrument was calibrated using a six-point 0.1-10 mg/L standard curve prepared from standard reference solution for individual metal, and the quality control solution were run during analysis to confirm the calibration. A spectrophotometer (Model Hach DR2000) for colour (in Platinum Cobalt unit) was used for colour determination. Experiments were run in triplicates to get a consistent average. Removal percentage for heavy metals and colour was achieved based on the different concentrations of heavy metals and colour, before and after experiment. Blank tests were conducted separately, using all adsorbent and distilled water (without metals and colour) to account for any heavy metals and colour that may be leached from each adsorbent. Batch experiments were repeated for charcoal and activated carbon. The weight of charcoal and activated carbon used were 34 g and 69 g respectively, which are equivalent to 40 mL each as volume.

Table 1 — General properties of adsorbent used in the study

Adsorbent	Activated carbon	Charcoal	Coconut shell carbon	Limestone
Particle size (mm)	2.36-4.75	2.36-4.75	2.36-4.75	2.36-4.75
pH value	7.26	7.12	10.42	-
Iodine value (mg/g)	590.22	317.33	310.98	241.17
VSS	68	68	77	0.28
Moisture (%)	<5.0	<5.0	<5.0	0.02

The final experiments examined the removal of heavy metals and colour using a mixture of adsorbent, i.e., charcoal + limestone, coconut shell carbon + limestone, and activated carbon + limestone with particle size between 2.36 and 4.75 mm and volume ratio of 1:1. All experiments were conducted separately. The total volume of adsorbent is 40 mL for the whole experiments and the respective weight is calculated based on the density of each adsorbent as given in Table 2. In order to establish whether the removal was due to pH, a set of batch experiment was repeated as above at pH value above 8, without any adsorbent addition.

Precipitation measurements

In order to determine the amount of metals precipitated, limestone particle was used in the experiment as follows. Precipitates were collected carefully by repeating the above experiments for three designated pH values of 5, 7 and 10, at a higher metal concentration (10 mg/L). Previous analyses have found that, it was really difficult to collect any precipitates at metal concentrations less than 10 mg/L.

To collect the precipitates, the balance of supernatant (after the metal concentration was sampled from the solution) was carefully pipetted out without disturbing the precipitates. The precipitates and limestone particle were then carefully rinsed in a

Table 2 — Parameters of adsorbent used in the experiment

Adsorbent	Density	Experiment with adsorbent shaken separately		Experiment with mixed adsorbent between limestone : carbon at ratio of 1:1					
	(kg/m^3)	Weight of adsorbent (g)	Volume of adsorbent (mL)	Weight of adsorbent (g)	Volume of adsorbent (mL)	Volume of limestone (g)	Volume of mixture (mL)	% Limestone by volume	% Carbon by volume
Limestone	2,508	100	39.87	50	19.94	-	-	-	-
Activated carbon	1,728	70	40.51	32.5	18.81	19.94	38.75	51.5	48.5
Coconut shell carbon	1059	45	42.49	20.5	19.36	19.94	39.30	50.7	49.3
Charcoal	851	35	41.12	17.5	20.56	19.94	40.50	49.2	50.8

beaker with distilled water and then filtered using cellulose acetate filter paper with pore size of 0.45 μm (the filter paper was dried in dessiccator beforehand). The filter paper was then dried in the dessicator, which was pre-vacuum for 20 min to ensure a good vacuum environment for drying. The drying may take one week until constant weight is achieved. The dried precipitates were carefully scraped from the paper, homogenized with mortar and pestle as detailed in the standard methods, and later sieved through 150 μm mesh. Some of the precipitates were accurately weighed and then digested using concentrated hydrochloric acid (HCl) in a digestion tube at 40°C for one hour and later at 140°C for 2 h as given in the standard methods[41]. Samples were diluted with distilled water to a designated volume, and analysed using AAS for all metals under considerations. The analyses were done in triplicates using different weights of precipitates and the results were averaged.

Results and Discussion

Calculation of removals

The percentage of heavy metals and colour removals at designated pH values was determined as follows:

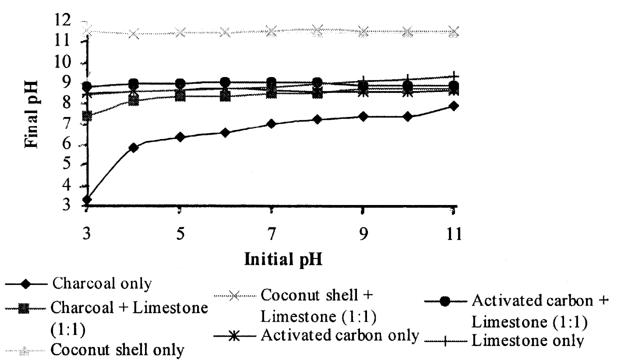

Fig. 1—The effect of adsorbent on sample's pH

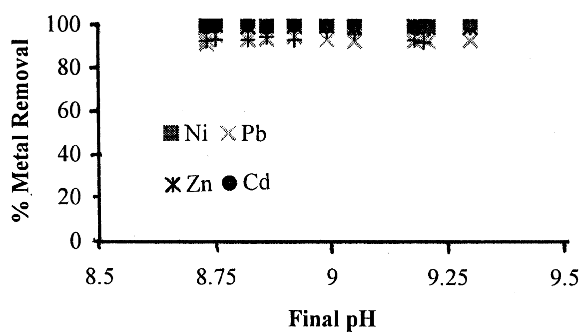

Fig. 2—Heavy metal removal for limestone adsorbent alone at metal concentration 2 mg/L

Removal percentage, % = $(C_1\text{-}C_2)/C_1 \times 100\%$

where C_1 = initial metal/colour conc. (in mg/L/PtCo) and C_2 = final metal/colour conc. (in mg/L/PtCo)

Removal (mass reduction) = $(C_3\text{-}C_4)/C_3 \times 100\%$

where C_3 = initial metal/colour mass (in mg/g) and C_4 = final metal/colour concentration (in mg/g).

Results

The density of adsorbent and other experimental parameters used in the experiment are given in Table 2. A plot of final pH against initial pH for the adsorbent with and without limestone is shown in Fig. 1. Fig. 2 gives a plot of heavy metal removal against final pH for limestone particle. Fig. 3 shows plot of Pb removal against pH value without any adsorbent. Fig. 4 shows the results of heavy metal removal against limestone and activated carbon. The objective is to determine the efficiency of limestone for heavy metals removal compared with an activated carbon. Fig. 5 shows the results of the effect of activated carbon and limestone mixture on metals removal. Figs 6-9 show the plots of heavy metal removal against final pH for charcoal alone, charcoal with limestone, coconut shell carbon alone and coconut shell carbon with limestone, respectively. Examples of significant effect of limestone on Pb removal are given in Figs 10 and 11. The effect of adsorbent in removing colour is given in Fig. 12 (percentage removal against initial pH) and Fig. 13 (percentage removal against final pH). Table 3 shows the amount of metals that were collected in the precipitates, followed by Fig. 14 that shows the plot of the precipitated metals.

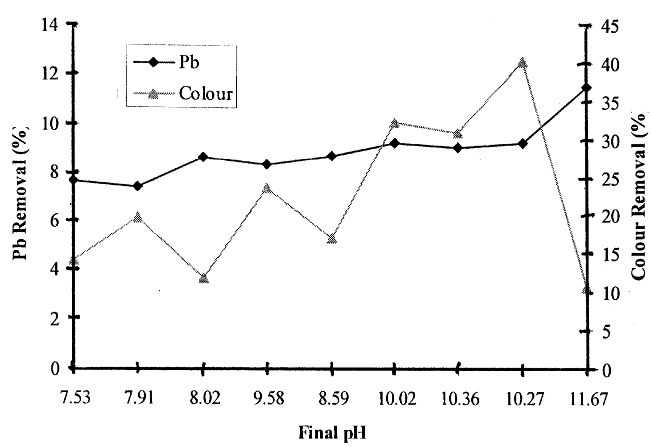

Fig. 3—Percentage of heavy metal and colour removal against final pH without presence of any adsorbent (example of metal is Pb)

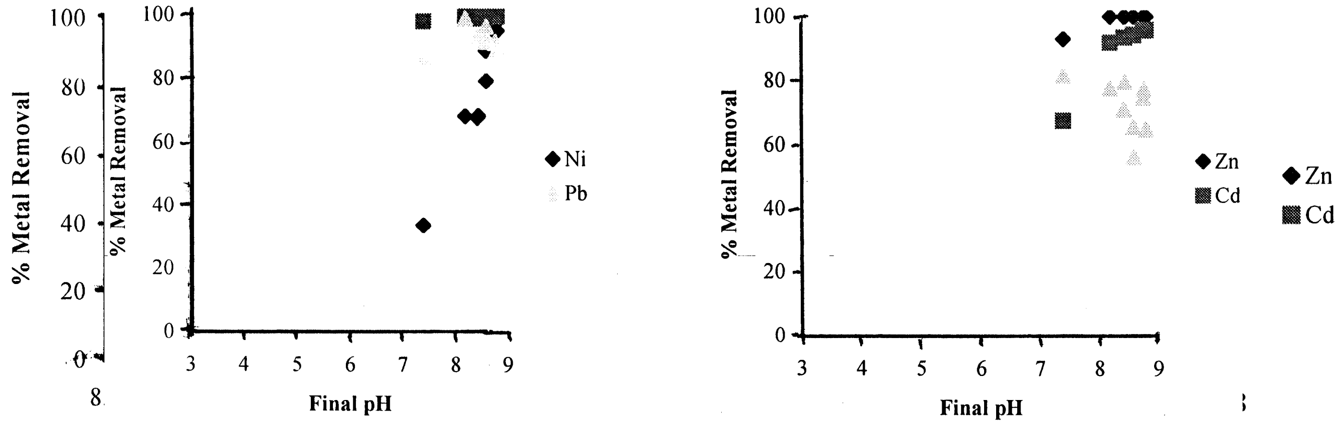

Fig. 7—Plot of heavy metal removal against final pH for a mixture of charcoal and limestone with ratio 1:1 by volume

Fig. 4—Plot of heavy metals removal against final pH for activated carbon alone

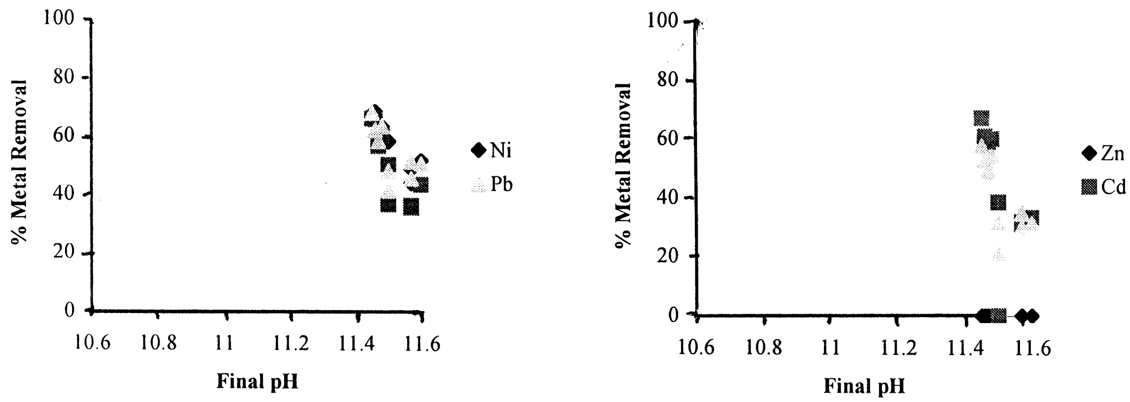

Fig. 8—Plot of heavy metal removal against final pH for coconut shell carbon adsorbent alone

Fig. 5—Plot of heavy metals removal against final pH for a mixture of activated carbon and limestone with ratio 1:1 by volume

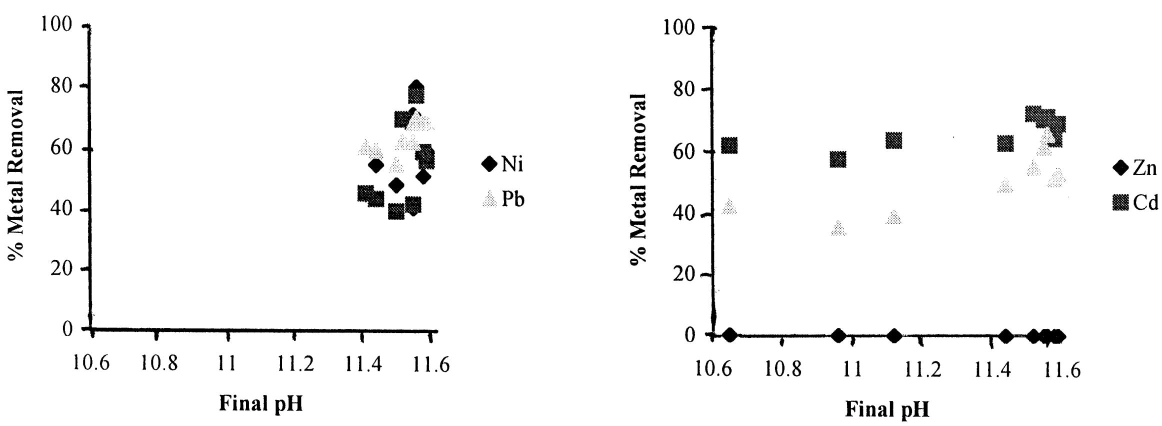

Fig. 9—Plot of heavy metal removal against final pH for a mixture of coconut shell carbon and limestone with ratio 1:1 by volume

Fig. 6—Plot of heavy metal removal against final pH for charcoal adsorbent alone

Effect of pH and adsorbents

Plot of final pH against initial pH in Fig. 1 shows that the final pH was higher for coconut shell carbon and its mixture with limestone (final pH exceeding 11). The former is mainly associated by the higher pH of coconut shell carbon as given in Table 1. This is followed by activated carbon with limestone (final pH between 8.8 and 9.1), activated carbon alone (final pH between 8.5 and 8.7), limestone alone (final pH between 8.8 and 9.3), charcoal with limestone (final pH 7.3-8.7 8). The limestone compared limestone). limestone sample.

In terms that, limest metals with final pH be removal without any adsorbent was fairly low (less than 12%), and greater at higher pH values, as shown

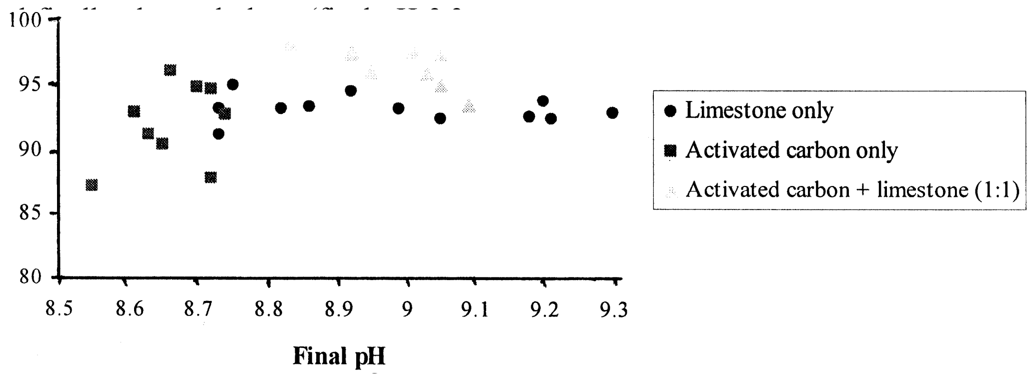

Fig. 10—Example of significant effects of limestone on Pb removal for limestone and activated carbon

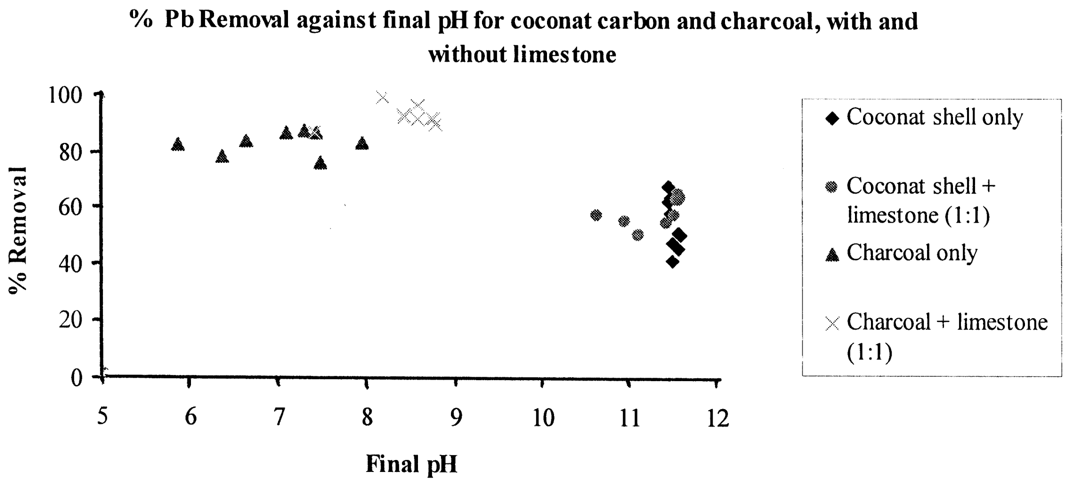

Fig. 11—Example of significant effects of limestone on Pb removal for coconut carbon and charcoal, with and without limestone.

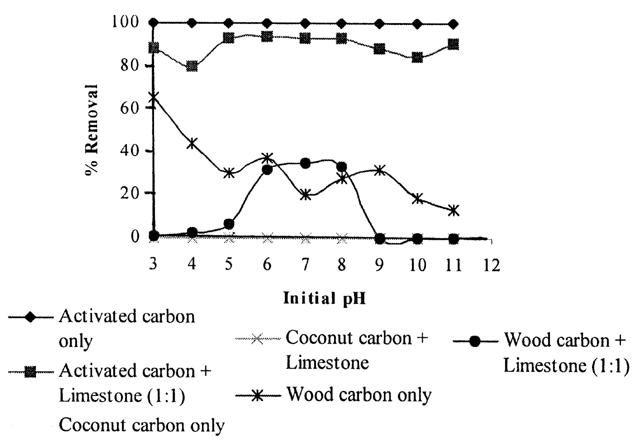

Fig. 12—The effect of various adsorbent on colour removal (Percentage removal against initial pH)

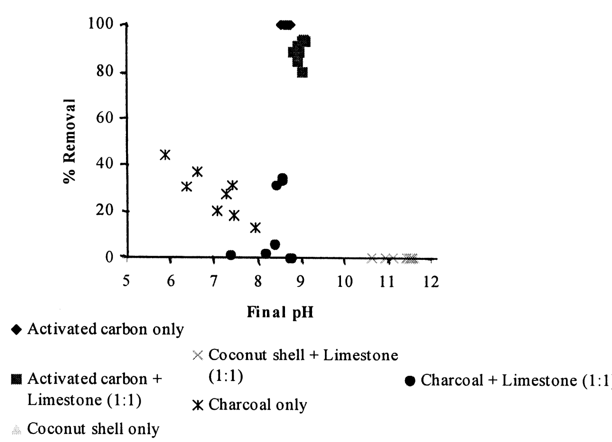

Fig. 13—The effect of various adsorbent on colour removal (Percentage removal against final pH)

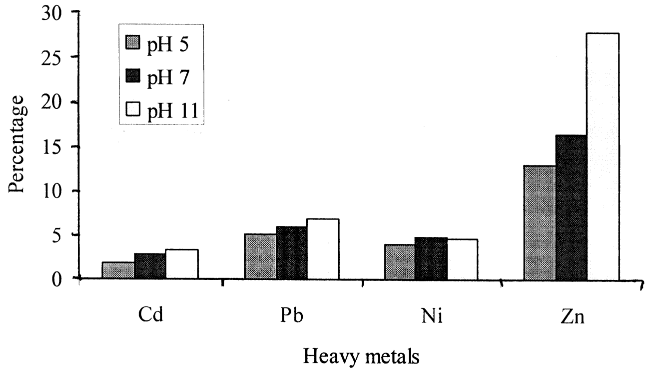

Fig. 14—Amount of heavy metals collected in precipitates at different pH values

Table 3 — Percentage of metal that was collected in precipitates

Initial pH	Final pH	% Heavy metal collected (Precipitation process)			
		Cd	Pb	Ni	Zn
5.0	8.73	1.84	5.10	3.86	12.95
7.0	8.86	2.75	5.96	4.69	16.34
10.0	9.21	3.30	6.85	4.58	27.82

in Fig. 3. This is mainly due to the precipitation of metals at alkaline conditions[38]. Activated carbon and a mixture of activated carbon with limestone removed heavy metals very efficiently with nearly 100% removal (0.24 mg/g) at a final pH of 8.8-9.1 as shown in Figs 4 and 5. Results for activated carbon alone shows that heavy metal removal was between 80 to nearly 100% ((0.216-0.24 mg/g) at a final pH of 8.54-8.74 (Fig. 4). A good removal of metals was achieved for Zn (nearly 100% or 0.24 mg/g), followed by Cd (96% or 0.23 mg/g), Pb (90% or 0.216 mg/g) and Ni (80 to 87% or 0.19-0.21 mg/g). This shows that limestone is very potential to be used as an alternative media to activated carbon.

Good removal was followed by charcoal and a mixture of charcoal with limestone by which the percentage of metal removal were about 65% (0.16 mg/g) (Fig. 6) and 80% (0.216 mg/g) (Fig. 7), respectively. Finally, the removal of heavy metal using coconut shell carbon and its mixture with limestone was 50-55% (0.12-0.13 mg/g), except for zinc (Figs 8 and 9). The adsorption capacity of the adsorbents and the associate isotherms are being studied.

Table 4 — Charcoal versus charcoal + limestone

One-way ANOVA for Pb removal efficiency

Source	DF	SS	MS	F	P
C4	1	464.0	464.0	30.37	0.000
Error	16	244.5	15.3		
Total	17	708.5			

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                                   Individual 95% CIs for mean
                                   based on pooled StDev
Level  N   Mean    StDev   +------+------+------+-----+
1      9   82.339  4.216   (---*---)
2      9   92.493  3.575                           (---*---)
                           +------+------+------+-----+
Pooled StDev =     3.909   80.0   85.0   90.0   95.0
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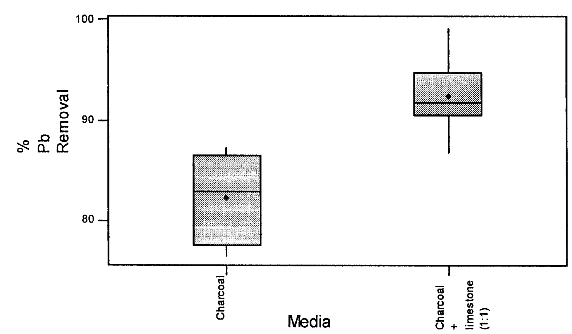

Experimental results showed that, better removal of metal was recorded with the presence of limestone at 2 mg/L metal, the concentration level for the scope of this paper. For example, the removal of Pb, with and without the presence of limestone as given in Figs 10 and 11. At final pH between 8.6 and 9.3, the removal of Pb using activated carbon with limestone was between 94 and 98% (0.23-0.24 mg/g), as compared to activated carbon alone (between 87 and 96% removal or 0.21-0.23 mg/g at pH 8.6-8.8), limestone alone (between 91 and 95% removal or 0.22-0.23 mg/g at pH 8.7-9.3), charcoal with limestone (87-99% removal at pH 7.4-8.8), charcoal alone (76-87% removal or 0.18-0.21 at 5.9-8), coconut shell carbon with limestone (50-65% removal or 0.12-0.16 mg/g at pH exceeding 11) and finally coconut shell carbon adsorbent alone (41-68% removal or 0.10-0.16 mg/g at pH exceeding 11).

The presence of carbon alone does not remove the metal as good as carbon and limestone are mixed. In other words, Figs 4-9 showed that a mixture of limestone with charcoal, coconut shell carbon and activated carbon (with ratio 1:1 as shown in Table 2) have resulted in higher percentage of heavy metal removal as compared to the percentage of heavy metal removal using charcoal, coconut shell carbon and activated carbon alone.

An example of an analysis of variance (ANOVA) between charcoal and charcoal mixed with limestone is shown in Table 4. The table indicates that there is significant difference between charcoal without limestone and charcoal with limestone in terms of the removal of Pb. The P value is 0.002 whereby the removal is better for the latter. Similarly, there is also significant difference in the Pb removal in case of activated carbon with limestone as compared to activated carbon alone. The significant value is P=0.001 with better removal achieved in the presence of limestone. This is due to the fact that when carbon was mixed with limestone, the removal was not solely due to adsorption process on the carbon, but was also helped by the limestone's properties which may be due to precipitation of metals as the case of Cu[42]. No significant difference was observed for limestone alone and activated carbon alone with P=0.278. This means, limestone performs as good as activated carbon for Pb removal. Coconut shell with and without the presence of limestone performs fairly equal. No significant difference was observed (P=0.199).

Plots of colour removal against final pH in Figs 12 and 13 show that activated carbon had successfully removed colour at almost 100%. On the other hand, the removal of colour in the presence of limestone has exhibited a slightly lower removal (over 80% as shown in Fig. 12) as compared to the use of carbon alone. For example, colour removal was slightly lower for a mixture of activated carbon and limestone, with a removal capacity of just exceeding 85%. This is probably due to the fact that the total surface area of adsorbent reduces as the adsorbent is now mixed with limestone. This better performance (over 80% removal of colour) is almost at par if not better than the performance of activated carbon alone as reported by McKay[43]. He found that activated carbon could adsorb between 30 and 80 % of its own weight of dye, depending on the dye.

The results also indicate that the removal of colour was influenced by the adsorbent and not solely by the pH (Figs 3 and 12) as the removal without any adsorbent was fairly low (less than 13%) as shown in Fig. 3. Even though McKay[43] showed that acidifying the effluent may slightly improved the adsorption capacities of most adsorbents, however, these increases were fairly small. The present results are in agreement with this statement that the removal of colour at a higher pH has shown a slight improvement (Fig. 3). The results are also in agreement with Zhang *et al*.[44] who indicated that higher pH favours colour removal but results in a much lower TOC adsorption capacity with activated carbon as adsorbent. The adsorption capacity of activated carbon strongly depends on the pH of the solution.

Percentage of colour removal using charcoal and a mixture of charcoal were not favourable with roughly 35% and 30%, respectively. Only a slight removal was recorded for coconut shell carbon and its mixture with limestone. By mixing the materials, the removal was decreased as shown in Figs 12 and 13. This shows that, limestone alone was not that effective in removing colour. When the amount of carbon was reduced by half (for a mixed adsorbent with limestone), the adsorption was decreased and hence the removal of colour was lower.

Results also showed that the removal of colour for coconut shell carbon was almost insignificant. Lower removal of heavy metals and colour recorded by charcoal and coconut shell carbon may be due to no activation process of carbon was undertaken. This was due to the fact that the temperature used was only 500°C with 4-5 min of retention time, and may not be sufficient as no activation process followed. This may lead to insufficient adsorption surfaces on the carbon. Further studies need to be conducted to get the optimum temperature with proper activation process of carbon. Even though, the removal of colour was slightly lower in the presence of limestone, the ability of limestone in removing heavy metals is significant. The advantage is that, the limestone could remove both parameters, i.e., heavy metals and colour as compared to the use of carbon only. The amount of activated carbon can also be reduced by mixing it with limestone, hence cutting the overall cost of treatment.

The results also indicated that the final pH for each adsorbent after the experiment has not changed significantly. The final pH for each experiment that used activated carbon, charcoal, and coconut shell carbon, a mixture of activated carbon with limestone, a mixture of charcoal with limestone and a mixture of coconut shell carbon with limestone was nearly the same at around 8.5, 7, 11.5, 9.0, 8.5 and 11.5. Therefore, it could be concluded that, the initial pH did not significantly affect the removal efficiency of heavy metals and colour as given in Figs 2-13. The only small effect shown was for the case of charcoal (Figs 1 and 7) which, at acidic final pH values, the percentage of metal removal were low (lower than 60%). At final pH exceeding 7, the percentage of metal removal was almost constant. These results were in agreement with Dilek and Bese[45] who stated that colour removal could not be improved with acid activation.

Precipitation of metals

Results of precipitates analysed by the AAS showed that, all metals were present in the precipitates, even though at very small concentrations (Table 3). It could be noticed that, more metals were collected for samples with higher pH values (pH 10) as compared to samples with pH 5. This is due to the fact that, generally, many metals will become insoluble at higher pH values[38]. It could be noticed that, at initial pH 5 (final pH 8.73), the amount of metal that could be collected was between 1.84 and 28.45% as compared to between 2.75 and 33.91% and 3.30 and 43.42%, respectively, for sample with initial pH 7 (final pH 8.86) and 10 (final pH 9.21). It could be concluded that, only a small amount of metals were precipitated from the solution, the remaining might be adsorbed to the surface of limestone.

Conclusions

It can be deduced from the experiments that carbon based adsorbent and limestone can be used to remove the heavy metal and colour from the wastewater samples. Good removal was achieved with the sequence of a mixture of activated carbon and limestone, limestone, activated carbon, a mixture of charcoal and limestone, charcoal, a mixture of coconut shell carbon and limestone and coconut shell carbon. On the other hand, the removal sequence for colour was activated carbon, a mixture of activated carbon with limestone, charcoal, a mixture of charcoal with limestone, coconut shell carbon and a mixture of coconut shell carbon with limestone. It can also be deduced from the experiments that the input pH was not significant in removing heavy metals and colour from the solution. Analysis on the precipitates has shown that, only a small amount of metals were present. Higher amount was recorded for metals with higher input pH values due to the insolubility of most metals at alkaline region. At initial pH 5 (final pH 8.73), between 1.84 to 28.45% metals were collected, as compared to between 2.75 and 33.91%, and 3.30 and 43.42%, respectively, for sample with initial pH 7 (final pH 8.86) and 10 (final pH 9.21). It could be concluded that, only a small amount of metals were precipitated from the solution, the remaining might be absorbed to the surface of limestone. It can also be suggested that the charcoal and coconut shell carbon require proper activation for better efficiency. Therefore, further studies are needed to examine an optimum temperature and contact time of adsorbent during activation process. Nevertheless, the use of limestone with carbon offers the advantage of being able to remove heavy metals and colour simultaneously. As activated carbon is quite high in cost, mixing of activated carbon with limestone will significantly reduce the cost of the overall process.

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