

# Chapter 9

## Conclusion

In the present work, the adsorption technique has been used for the abatement of hazardous metals from contaminated water. The present study on adsorption of  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions from aqueous solutions using novel adsorbents suggested the following conclusions:

- The SEM micrograph of composite revealed that small particles consisting of platelets conglomerated with the larger particles. The fluffy layered sheet structure transformed into the rugged and foliated layered structure after adsorption. The ATA was made up of fine particles (before adsorption), that did not possess regular, fixed shape and size. After adsorption, heterostructure showed agglomerated appearance. The SEM micrograph of AC showed that the surface had protrusions that run through the biomass matrix. The particle size distribution was diasporic, indicating that the activated carbon particles came in a wide range of forms and sizes. Another feature was the activated carbon particles' rough and layered surface, which resembled a loose sponge. The surface structure of mould was slack and porous, with a high specific surface area and sufficient adsorption zone. As a result, it was expected to have a high adsorption capacity. Prior to adsorption, the surface had irregularities that aid in increasing surface area. The surface of the mould became saturated after metal ion adsorption. The surface of mould had schistose structures, preferable for the adsorption of  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions.

- The findings of EDX showed that peaks of Na, Mg, Ca, Al and Fe in composite material were due to the inherent characteristics of bentonite clay and red ochre and also, ATA primarily consisted of C and O and minimal quantity of Al, Mg, Ca, Na, Si, N, K, P and S. The EDX of AC showed the presence of C, O, Na, Al, S, Cl and K. The EDX of mould showed the presence of K, O, Fe, Mg, Al, and Si.
- The FTIR of composite showed the presence of Al-AlOH and Al-MgOH in the aluminium rich octahedral centers of bentonite, bending vibration of the H-O-H group and Si-O stretching of silica and quartz. The FTIR of ATA showed the presence of O-H stretching of the carboxylic groups, N-H stretching and C=O stretching of syringaldehyde. The FTIR spectra of TG and AC revealed the presence of alcohols and phenols in the structure via the O-H stretching vibration. TG indicated the existence of aromatic ring stretching (phenolic groups). In both TG and AC, the C=O stretching vibrations indicated the presence of a carbonyl group in ketones, phenols, carboxyl acids and aldehydes. The S=O stretching was observed for both TG and AC. Both TG and AC exhibited C-H and C-OH stretching vibrations. This was due to the occurrence of multiple functional groups on the surface of TG and AC. Additionally, aryl halide ( $C_6H_5-X$  or  $Ar-X$  where  $X = F, Cl, Br, \text{ and } I$ ) and alkenes ( $C=C$ ) were found on the surface of TG and AC. The missing, shifting or presence of bonds indicated that AC exhibited chemical change following activation. Surface pore formation was exacerbated as a result of the removal of many functional groups in AC. The FTIR of mould showed the presence of stretching vibrations of O-H groups and is associated to alcohols and phenolic compounds. It also possessed the water molecule's O-H bonds bending within the silicate matrix and also, stretching vibrations of Si-O-Si, Si-O-Al and Al-O on tetrahedral and octahedral sheets. It also had Al-Mg-OH stretching, which implied the presence of quartz.
- XRD study revealed that composite is composed of quartz, alumina and hematite. The XRD graph of ATA revealed that the substance is partly amorphous and should find application as an adsorbent. The XRD pattern of AC indicated the amorphous

behaviour of graphitic carbon (002) and (101). Calcite ( $\text{CaCO}_3$ ) has been identified in AC. Microbiologically precipitated calcite has a wide range of applications, including soil recovery, soil stabilization, and concrete restoration. Peaks revealed the existence of whewellite in AC. The XRD pattern of mould showed the presence of montmorillonite (M), illite (I), quartz (Q) and feldspar (F).

- The BET surface area of composite, ATA and AC was found to be  $447.31 \text{ m}^2/\text{g}$ ,  $71.35 \text{ m}^2/\text{g}$  and  $1270 \text{ m}^2/\text{g}$  respectively.
- The result of ultimate analysis for composite indicated 39.03 % carbon, 14.46 % nitrogen, 1.48 % hydrogen and 0% sulphur in the composite. These results showed the existence of organic matter within the composite (high carbon content). These findings enhanced the composite application as a metal ion scavenger for heavy metal ions. The proximate analysis of ATA quantified 55.22% fixed carbon, 8.51% moisture, 14.78% ash and 21.49% volatile matter. The lower ash content in ATA indicated that adsorbent was properly prepared. The ultimate analysis of ATA showed 38.47% C, 1.89% H, 49.21% O, 10.43% N. The proximate analysis of TG quantified 67.3% fixed carbon, 18.3% moisture, 0.7% ash and 13.7% volatile matter. In TG, high carbon and low ash concentration suggested that it could be an effective carbon precursor for producing AC. The inclusion of organic components contributed to the greater volatile matter content of TG. The mould was found to have a low moisture (0.49%) and ash (4.5%), and a high volatile matter (95.01%) content based on the proximate analysis
- The bulk density of ATA and AC was calculated as  $0.47 \text{ g}/\text{cm}^3$  and  $0.42 \text{ g}/\text{cm}^3$ . A suitable adsorbent has a lower bulk density value. The occurrence of micropores in the structure was reported through bulk density. The apparent bulk density of the ATA was in the range of acceptable limit recommended by ASTM, i.e.,  $0.42 - 0.52 \text{ g}/\text{cm}^3$ .
- The pHzpc of the composite was found to be 5.2. The composite surface is negatively charged above this pH value which supports the removal of cations. The

$\text{pH}_{zpc}$  of ATA was found to be 5.07 in the present study. It means beyond this value; the surface will be negatively charged. The  $\text{pH}_{zpc}$  value obtained for AC was 8.56. At a value smaller than 8.56, this value indicated that AC is positively charged.

- The study of adsorption dynamics for novel adsorbent using dimensionless numbers for  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ions showed that adsorption on the surface of AC and mould was transfer controlled, the process is diffusion controlled for ATA and for composite, the adsorption was diffusion controlled for  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions and mixed diffusion and transfer controlled for  $\text{Zn}^{2+}$  ions.
- The adsorption of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ions was based on film diffusion using AC and composite, pore diffusion using ATA and mould as evidenced from values of film and pore diffusivity coefficients.
- Both the experimental and theoretical values for novel adsorbent seemed to be in agreement with each other showing a high regression coefficient ( $R^2$  value in range of 0.95 - 0.99) for AC,  $R^2$  of 0.98 for ATA,  $R^2$  of 0.89 - 0.92 for composite and  $R^2$  of 0.98 for mould.
- Experimental results for AC as adsorbent indicated that the PSO reaction kinetics provided the best description of the data. The isotherm study indicated that adsorption data correlated well with Freundlich isotherm model. Isotherm and kinetics study for ATA as an adsorbent showed supremacy of Langmuir and PSO describing the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ions. The adsorption of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ions on the surface of composite indicated better goodness of fit for Langmuir isotherm together with PSO model (chemisorption mode). The best fit of the experimental data for mould were for Langmuir isotherm and PSO kinetic model, which demonstrated the chemisorption of metal ions with monolayer coverage.
- The adsorption of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ions on composite material and ATA followed the same trend as electronegativity, i.e.,  $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+}$ . Multi-metal systems using AC function in the same way with nickel as the most efficient adsorbate and zinc as the least.  $\text{Ni}^{2+}$  ions (0.069 nm) have the lowest ionic radius of all ions,

implying faster adsorption. The second most adsorbed metal was  $\text{Cu}^{2+}$  ions (0.073 nm), followed by  $\text{Zn}^{2+}$  ions (0.074 nm). This indicated that the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ions on AC followed the opposite trend of ionic radius, i.e.,  $\text{Ni}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$ . The results were in the order of  $\text{Ni}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$ . This was due to ion exchange in the adsorption of cations, a cation with a smaller hydration radius adsorbs more quickly due to its greater ability to attract electrons. The hydration radius is in order of  $\text{Ni}^{2+}$  (4.04) <  $\text{Cu}^{2+}$  (4.19) <  $\text{Zn}^{2+}$  (4.30).

- Thermodynamic study on AC, ATA and composite indicated the endothermic and spontaneous nature of the adsorption. The results revealed non-spontaneous endothermic adsorption of  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions onto mould.
- The optimum parameters for AC were pH 9, initial  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ions concentration 100 mg/L, contact time 30 minutes, temperature 35°C and AC dose 0.10 g. The optimum parameters for ATA were pH 6, initial  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ions concentration 100 mg/L, contact time 210 min, temperature 35°C and ATA dose 1 g. The optimum parameters for composite as adsorbent were observed as pH 6, composite dose 1 g, initial  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ions concentration 100 mg/L, temperature 35°C and contact time 60 minutes. The optimum parameters for mould were pH 6, initial  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ions concentration 50 mg/L, contact time 30 min and temperature 35°C.
- For composites, ion exchange and surface complexation were the primary adsorption mechanisms; for ATA, ion exchange, solvation, and complexation were all involved; for AC, ion exchange, hydrogen bonding, and complexation were all major adsorption mechanisms; and for mould, ion exchange, electrostatic adsorption, and complexation were all major adsorption mechanisms for the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ions. Furthermore, diffusion was identified as an adsorption mechanism in the adsorption dynamics investigation for all novel adsorbents except AC and mould, which were transfer controlled.
- The present study showed that AC and ATA is a potential alternative for the removal

of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ions effectively from metal contaminated water. The composite developed can be of enormous industrial relevance. A thin coating of the mould material inside the water tank will reduce metal concentration in water considerably. At the end, the concentration of metal ions in residual solution below the permissible limit was achieved in the present study by using these novel adsorbents.