



Biosorption of Hg(II) ions, Congo red and their binary mixture using raw and chemically activated mango leaves

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Abstract

This study reports the investigation performed by comparing the ability of raw and treated mango leaves powder (with potassium persulphate, $K_2S_2O_8$) to adsorb Hg^{2+} , Congo red dye and their binary mixture from their aqueous solutions through batch experiments. Both adsorbents were characterized by Fourier-transform infrared spectroscopy to reveal the active sites of both adsorbent. The experimental parameters such as pH, contact time, adsorbent dosage, initial concentration and temperature were investigated. The maximum removal of Hg^{2+} , Congo red and binary mixture obtained were 42.86%, 54.72% and 62.5% using raw mango leaves powder and 64.29%, 81.25% and 63.82% using treated mango leaves respectively at pH 7. The experimental data better fit the Langmuir isotherm model for binary mixture adsorption on both adsorbent, the Freundlich isotherm model for Congo red dye adsorption on raw adsorbent and Hg^{2+} adsorption on both adsorbents, the Brunauer–Emmett–Teller isotherm model for Congo red adsorption onto the treated adsorbent. Kinetic data were best fit to a pseudo-second-order rate equation except the adsorption of Congo red onto untreated adsorbent that supported pseudo-first-order rate equation. Thermodynamic parameters shows that adsorption of binary mixture onto treated adsorbent and Hg^{2+} adsorption on both adsorbents were spontaneous and endothermic in nature while adsorption of binary mixture onto untreated adsorbent and Congo red adsorption on both adsorbents were non-spontaneous and endothermic in nature between temperatures of 30 and 60 °C. This study revealed a great potential of raw and treated mango leaves in the effective removal of Hg^{2+} , Congo red and their binary mixture from waste water.

Keywords Raw mango leaves powder · Treated mango leaves powder · Hg^{2+} adsorption · Congo red adsorption · Binary mixture adsorption · Experimental parameters · Thermodynamic parameters

Introduction

Rapid increase in civilization and technological advancement in industrialization has led to the release of effluents containing heavy metals and dyes which exist in aqueous waste streams of many industries, thereby resulting in frequent and severe infections in the living organisms that accumulated them (Singh and Arora 2011). This has led to the establishment of environmental regulations with regard to the quality of wastewater for the industries to comply with in order to safeguard the health of present and future generations.

Mercury for instance, enters into the environment as a pollutant from coal-fired power stations, residential coal, industrial process and waste incinerator (Gadd 2009). It is transformed by bacteria into methyl mercury (CH_3Hg) which is then bioaccumulated and biomagnified. The effects on exposure to it include genetic defects, neurological and behavioral disorders, tremors, insomnia, memory loss, etc. On contrary, Congo red (CR) containing effluents which are generated from textiles, printing and dyeing industries (Sharma and Janveja 2008) metabolizes to benzidine, a known human carcinogen and exposure to it has been known to cause an allergic reaction (and possibly, anaphylactic shock) (Jyoti and Beena 2008).

This recurring environmental pollution thus needs an urgent solution. And for this reason various physical, biological and chemical methods like membrane-filtration, adsorption techniques, fungal decolorization, microbial degradation, bioremediation, and oxidation have been

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put into use, but the pitfall in them is that they are not cost-effective and economically viable (Eccles 1999). But should this problem be left unsolved and its consequences be managed? This will eventually create disorders in the beings of the universe. Therefore, a more sustainable method called “Biosorption” has been discovered. This method which involves the passive uptake of toxicants from aqueous solutions by dead/inactive materials derived from biological sources, is an alternative and effective technology for removing these target substances from aqueous solution due to its low operating cost, selectivity, excellent performance, eco-friendly nature and short operation time (Gadd 2009).

However, studies have shown that plant materials could be pretreated or modified before adsorption to improve the percentage removal efficiency of heavy metals and dyes such as EDTA modified peanut shells (Liu et al. 2010) and acid activation mango leaf (Tabrez et al. 2011; Ashraf et al. 2010). The main components in mango (*Mangifera indica*) leaf being cellulose, hemicelluloses, pectins and lignin provide different functional groups such as hydroxyl, carboxylic, amino and nitro groups responsible for adsorption sites (Sheen 2011). Most of the recent reported works have investigated removal of a single pollutant system while only a few have focused on simultaneous removal of both dyes and heavy metals from their mixtures by adsorption (Thomas 2016). Mango (*Mangifera indica*) leaf powder has been reported effective to remove a single pollutant system such as Rhodamine B dye (Tabrez et al. 2011), and Cu^{2+} (Sheen 2011). However, in this study, mango leaves powder was activated by chemical modification process using a strong oxidant “potassium persulphate ($\text{K}_2\text{S}_2\text{O}_8$)” so as to increase oxygen-containing functional groups on mango leaves powder and to enhance its adsorption capacity (Xue et al. 2012). To the best of the authors’ knowledge, this is probably the first report on the use of potassium persulphate in the chemical modification of an agro-based adsorbent for the treatment of binary pollutant matrix.

Therefore, the aim of this study is to investigate the removal of CR and Hg^{2+} in aqueous solutions of their binary matrix using untreated and modified mango leaves powder as bioadsorbent. The effect of solution pH, contact time, initial concentration, adsorbent dose and temperature were investigated in the removal of Hg (II) ions and CR dye by raw mango leaf powder and compared with the pre-treated mango leaf powder. Adsorption kinetics and thermodynamics were fitted to the experimental data and biosorption mechanism was proposed. The research was conducted at Bioremediation and Applied Biotechnology Laboratory, Department of Chemistry, Federal University of Technology Akure, Nigeria between September 2016 and November 2017.

Materials and methods

Materials

All chemical reagents used were of analytical grade and purchased from Sigma-aldrich, UK. The mango leaves were obtained from mango trees located around Obanla campus at the Federal University of Technology, Akure (FUTA), Ondo State, Nigeria. The Fourier-transform infrared (FT-IR) spectrum ($4000\text{--}500\text{ cm}^{-1}$) was recorded by Perkin Elmer 3λ spectrometer. All pH measurements were done using a pocket pH tester (pH-107).

Preparation and pre-treatment of raw mango leaves powder

Mango leaves were collected and washed, submerged in the acid rinse (0.01 M HCl) and then rinsed with de-ionized water. The leaves were then dried under sunlight for 3 days and then oven-dried at $105\text{ }^\circ\text{C}$ in the laboratory oven (Model no: DHG-9101.1SA) until it became crisp. The dried mango leaves were ground to a fine powder, sieved to $250\text{ }\mu\text{m}$ mesh and stored in an air-tight container named untreated mango leaves powder (UMLP). The method described by Xue et al. (2012) was adopted in the treatment of pulverized mango leaves. This was stored in an air-tight container named treated mango leaves powder (TMLP).

Adsorbate preparation

Preparation of mercury (II) ions stock solution

Exactly 2000 mg/L Hg(II) ions stock solution was prepared by dissolving accurately 1 g of mercury (II) chloride in 500 mL distilled water with appropriate dilution of the stock solution.

Preparation of Congo red dye stock solution.

About 2000 mg/L CR solution was prepared by dissolving accurately 1 g of CR dye powder in 500 mL distilled water. Then serial dilutions were taken to obtain desired concentrations of CR dye solution.

Batch adsorption studies

The batch adsorption studies were carried out by weighing 0.1 g of each adsorbent (UMLP and TMLP) on an analytical balance readability of 0.0001 g into different 250 mL Erlenmeyer flasks containing either 50 mL of 60 ppm Hg(II) solution for Hg^{2+} determination, 50 mL of 60 ppm CR dye

solution for CR dye determination or addition of 50 mL of 60 ppm CR dye solution and 50 mL of 60 ppm Hg(II) solution to make binary mixture for Hg²⁺ and CR determination. The effect of pH on biosorption rate was investigated on a pH range of 4–9, which was adjusted by micro-additions of 0.1 M HCl and 0.1 M NaOH and then the solution was agitated on an orbital shaker at 100 rpm for 2 h. After agitation, each sample was filtered using Whatman filter paper no. 42 and the supernatant was refrigerated in the refrigerator (Midea HD-276F) until the metal analysis and dye analysis were done.

For optimization of contact time, 0.1 g of each sample was taken at predetermined time intervals (30–120 min) at pH 7. The best amount of each adsorbent was determined by changing each adsorbent dosage from 0.05 g to 0.25 g at pH 7 and was agitated for 30 min. The initial concentration of each adsorbate solution taken for this study was 30, 60, 90 and 120 mg/L at pH 7 and was agitated for 30 min. Thermodynamic studies were carried out at 30, 40, 50, 60 and 70 °C in a water bath shaker under optimum pH, contact time, adsorbent dosage and initial concentration.

Adsorbate analysis.

The residual Hg²⁺ and CR dye concentrations in their respective supernatant were analyzed by UNICAM UV HELIOS β at a λ_{max} of 497 nm and 488 nm for CR dye and Hg²⁺, respectively.

CR sample was read colorimetrically without further adding of reagent because of the conjugated compounds presence.

Working standards for Hg²⁺ ions were prepared as described by Ahmed and Alam (2003) and was read colorimetrically by pipetting 120 μL of mercury (II) sample with respective addition of 240 μL diphenylthiocarbazone (1.45×10^{-3} M), 30 μL of H₂SO₄ (4.5 M), 1500 μL of 1, 4-dioxane and 1110 μL of distilled water.

Results and discussion

Characterization of the adsorbents

The FTIR spectra of the raw, as well as treated mango leaves powder was obtained with resolution range of 500–4000 cm⁻¹ and are shown in Figs. 1 and 2 respectively. The broad and intense peak of UMLP at 3408.33 cm⁻¹ and 3360.11 cm⁻¹ were attributed to the stretching of OH group due to inter- and intra-molecular hydrogen bonding of large macromolecules such as alcohols or phenols as in pectin, hemicelluloses, cellulose and lignin (Igbal et al. 2008); it was shifted after treatment to 3392.90 cm⁻¹. The peak observed at 2920.32 cm⁻¹ and 2850.88 cm⁻¹ for UMLP were associated with the C–H stretch of methyl, methylene and methoxy groups. It was shifted after treatment to 2920.32 cm⁻¹ and 2852.81 cm⁻¹, respectively. The peak observed at 1720.56 cm⁻¹ for UMLP was associated with the C=O stretch of aldehydes and saturated aliphatic; it was shifted for TMLP to 1728.28 cm⁻¹. The peak at 1620.26 cm⁻¹ indicated the presence of carbonyl group (C=O), whereas in TMLP, the peak was observed at 1631.83 cm⁻¹ representing N–H bend of primary amine. The

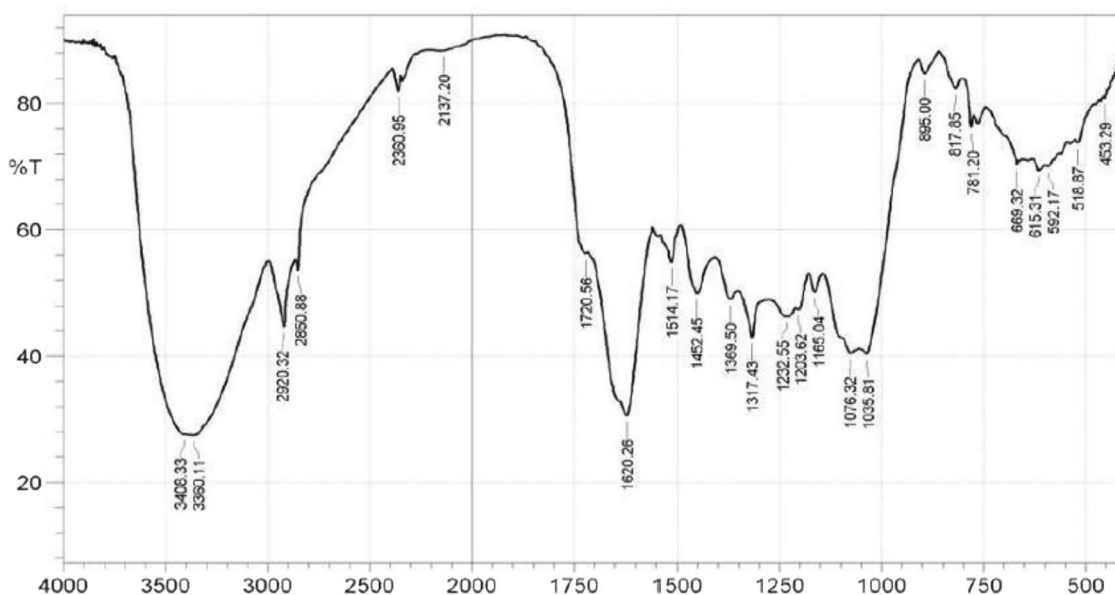


Fig. 1 FTIR spectrum of Raw Mango leaves powder (UMLP)

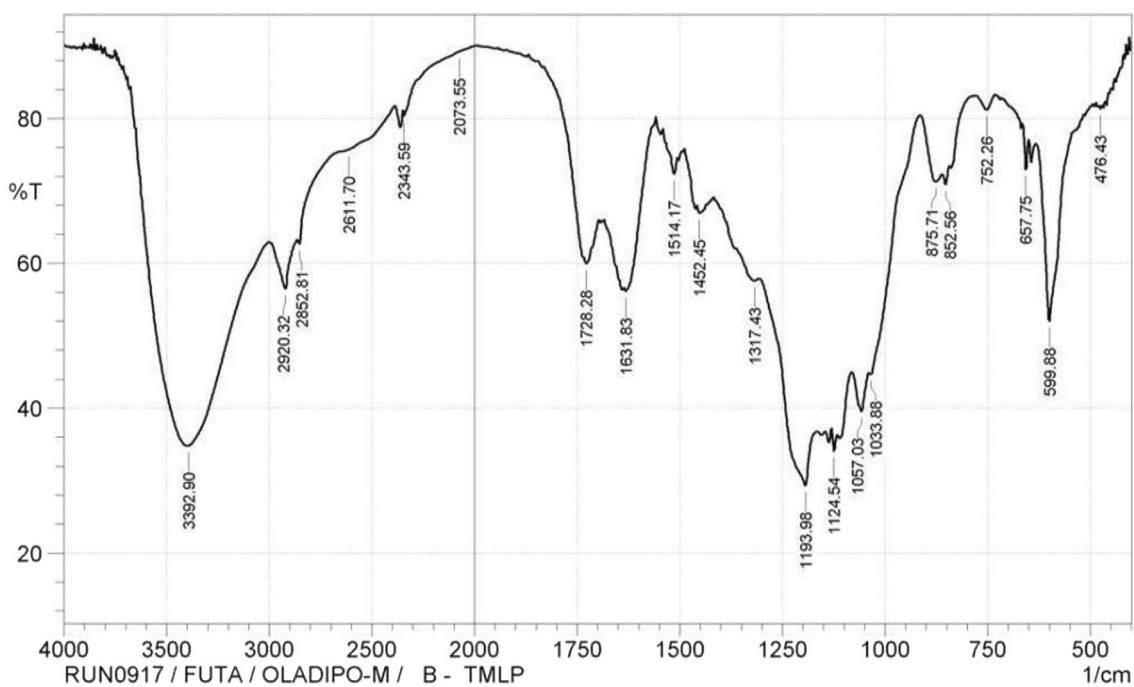


Fig. 2 FTIR spectrum of Treated Mango Leaves powder (TMLP)

peak observed at 1369.50 cm^{-1} for UMLP indicated C–H rock of alkanes. Peaks at 1317.43 cm^{-1} , 1452.45 cm^{-1} and 1514.17 cm^{-1} for both biosorbents representing C–N stretch of aromatic amines, C–H bend of alkanes and N–O (nitro groups), respectively. The peak at 1232.55 cm^{-1} indicated C–N stretch of aliphatic amine and it was confirmed once again at peak of 1203.62 cm^{-1} , whereas it was shifted to 1193.98 cm^{-1} for TMLP that indicate C–O stretch of alcohols, carboxylic acids and ester. The peaks at 1165.04 cm^{-1} and 1076.32 cm^{-1} confirmed the presence of C–N stretch of the aliphatic amine, in which the peaks are shifted after treatment to 1193.98 cm^{-1} and 1057.03 cm^{-1} , respectively. The peak at 1033.88 cm^{-1} confirmed the presence of C–N stretch of the aliphatic amines. The peaks at 895.00 cm^{-1} and 817.85 cm^{-1} indicate the presence of C–H “oop” of the aromatic compound, whereas it is shifted for TMLP to 875.71 cm^{-1} and 852.56 cm^{-1} , respectively, in which they indicate the presence of =C–H bend of alkanes and =C–H bend of aromatics. The intense peak at 599.88 cm^{-1} of TMLP was assigned to the asymmetric bending of SO_4 group while the peak at 476.43 cm^{-1} corresponded to the symmetric bending of SO_4 group (Periasamy et al. 2009). Results showed that there were changes in some chemical functional groups of TMLP biosorbent.

Effect of pH

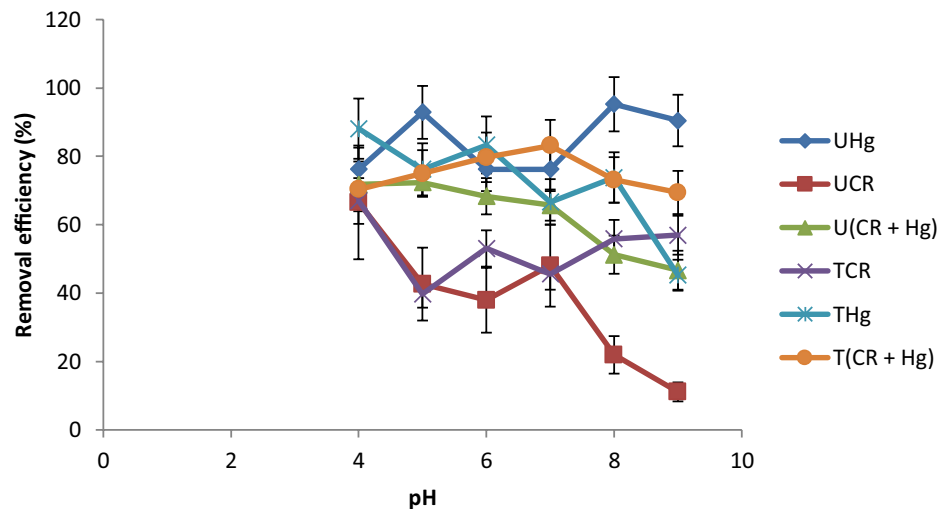
An important factor influencing the adsorption process, affecting the surface charge of the adsorbents and also

influences the degree of ionization of metal/dye ions in solution which affects the availability of active sites on the adsorbent is the pH of the solution.

The percentage removal of Hg^{2+} , CR dye and (Hg^{2+} and CR) binary solution by each adsorbent (UMLP and TMLP) with pH ranged from 4 to 9 is shown in Fig. 3. The biosorption of these adsorbates from the aqueous solutions occurred majorly by electrostatic forces (Anirudhan et al. 2012).

It was observed that the percentage removal of Hg^{2+} increased from 76.19% to 90.48% using UMLP biomass and decreased from 88.10% to 45.24% using TMLP biomass by increasing the pH from 4 to 9. The increment may be due to the fact that at lower pH, the surface functional groups of UMLP biomass becomes protonated as a result of the predominance of HgCl_2 (Hg^{2+}) and high concentration of H^+ species that makes less available sites for Hg^{2+} adsorption. In addition, at higher pH, the Hg^{2+} adsorption increased due to increase in the presence of $\text{Hg}(\text{Cl})\text{OH}$ and $\text{Hg}(\text{OH})_2$ species that allowed Hg^{2+} to be adsorbed (Anagnostopoulos et al. 2012). The decrease in the percentage removal of Hg^{2+} by TMLP biomass was as a result of the fact that at higher pH, the H^+ tends to react with HSO_4^{2-} and HSO_5^- formed from reactions that occurred between persulphate anion and water which makes the surface functional groups of TMLP biomass to be available for binding with Hg^{2+} while at lower pH, the H^+ tends to react only with HSO_4^{2-} only and also protonated the surface functional groups of TMLP biomass a little bit which results to drop in the percentage removal

Fig. 3 Effect of pH change on removal efficiency (%) of CR dye, Hg^{2+} and (Hg^{2+} and CR) binary solution



efficiency of Hg^{2+} by TMLP. At higher pH (particularly above pH 9), deprotonation of the functional group on the adsorbent occurs thus making them to act as if they were negatively charged moieties. This negatively charged particles are easily attracted to positively charged metal ions. In addition, at higher pH, metal precipitation occurs due to the formation of metal hydroxide complexes when the pH of the solution is higher than the pH of the point of zero charge (Abdel-Ghani and Ghadir 2014). The sudden increase in the percentage removal efficiency of Hg^{2+} by UMLP biomass at pH 5 and for TMLP biomass at pH 6 indicated the adsorption by both ion exchange and surface complexation (Taha et al. 2017). A slight decrease in the removal efficiency (%) of Hg^{2+} by UMLP biomass at pH 9 may be due to the fact that Hg^{2+} adsorbs other anions species in the aqueous solution as a result of the saturation of active sites while, a sharp decrease in the removal efficiency of Hg^{2+} by TMLP biomass at pH 9 was as a result of formation of HSO_4^{2-} and SO_4^{2-} by persulphate anion at alkaline medium in which Hg^{2+} prefers reacting with SO_4^{2-} in the solution to the surface functional groups of TMLP biomass.

The percentage removal efficiency of CR dye decreased from 66.52% to 11.11% for UMLP and decreased from 66.94% to 56.94% for TMLP in the working pH 4–9. At lower pH, the surface of the adsorbent become more protonated which make the anionic dye to bind with the carbon at the surface of the adsorbent easily and at higher pH, hydroxyl ion increases which competes with the anionic dye for sorption site. The lower adsorption of CR dye (21.94% and 11.11%) at pH 8 and 9 respectively by UMLP biomass may be due to an abundance of hydroxyl ion which competes with the dye anions for the adsorption sites and the higher adsorption of CR dye (55.83% and 56.94%) at pH 8 and 9, respectively by TMLP biomass may be due to the fact that

persulphate anion tends to react with the hydroxyl ion and reduces its competing power with the anionic dye which then makes the sorption site available for anionic dye.

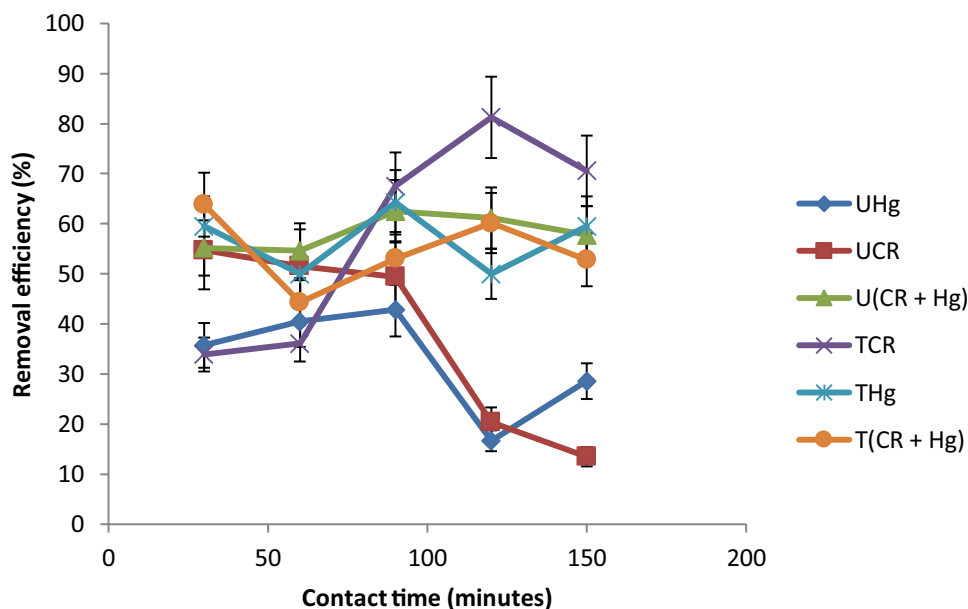
For the (Hg^{2+} and CR) binary solution, the percentage removal efficiency decreased from (71.79% to 46.7% as well as 70.34% to 69.43%) for UMLP and TMLP, respectively. High adsorption of the binary mixture was due the ability of Hg (II) ions to form covalent bonds with the anionic group on the adsorbents while the low removal could be attributed to competition for the anionic groups between CR dye molecules and the amine groups on the adsorbents (Yang and Feng 2010).

By comparing the binary mixture adsorption by various adsorbents, it was observed that TMLP has relative maximum removal efficiency (83.11%) at pH 7. Therefore, in the subsequent work, experiments were carried out at fixed optimum of pH 7.

Effect of contact time

The effect of contact time on the removal of Hg^{2+} , CR dye and the binary mixture are depicted in Fig. 4. The adsorption efficiency of Hg^{2+} using UMLP increased with time from 30 min (35.71%) to 90 min (42.86%), the time of maximum adsorption and then decreases to 16.667% at 120 min. Later, it increases at 150 min (28.57%). This is because as biosorption proceeds at the start of experiment, the free binding sites becomes occupied reducing rate of biosorption until it approaches equilibrium at 90 min (42.9%) due to the saturation of active sites with Hg^{2+} (Zenasni et al. 2014). The later increment in the uptake capacity at 150 min signifies possible decrease in rate of desorption with respect to the time. For TMLP there was a fast sorption of the Hg^{2+} in the first 30 min (59.524%). This is due to the free negatively charged ions at the surface of the adsorbent having the ability to bind

Fig. 4 Effect of contact time on removal efficiency (%) of CR dye, Hg^{2+} and (Hg^{2+} and CR) binary solution



with Hg^{2+} (Gupta et al. 2009). At 60 min, a 50% decrease in Hg concentration was observed which may be due to the contribution of interfering ions that competed with Hg^{2+} for binding on the adsorbent's surface. Then the uptake capacity increased from 60 min to the equilibrium contact time of 90 min (64.286%) after which the percentage removal decreases due to unavailability of active site for Hg^{2+} sorption at 120 min and increases at 150 min due to the available active sites for adsorption process.

With the use of UMLP, adsorption of CR dye increased and reached equilibrium for the first 30 min (54.72%) and later decreased to 13.472%. This may probably be due to the availability of a larger surface area of the adsorbent at the beginning for the adsorption of dyes ions (Thomas 2016) and gradual decrease occurred because the remaining vacant sites find it difficult to occupy. Using TMLP biomass, there was a rapid removal of CR dye in the first 30 min (33.89%) and it proceeded slowly until equilibrium time at 120 min (81.25%) and then decreased to 70.56%. The rapid sorption occurred because most of the active sites on the adsorbent's surface were ready to bind with CR dye in the wastewater. The slower rate of removal at the later stage can be as a result of the diffusion of the dyes into the inner part of the adsorbent since the external surface has been occupied by the molecules of the dye. The equilibrium is achieved as a result of the binding sites that became exhausted. The percentage removal gradually slowed down due to the repulsive forces between the molecules on the adsorbent and the bulk phase (Wu 2007).

The removal efficiency of CR dye from (Hg^{2+} and CR) binary solution at contact time in the range of 30–150 min tends to increase from 14.86% to 23.89% for UMLP and decrease from 77.64% to 65.14% for TMLP, whereas the

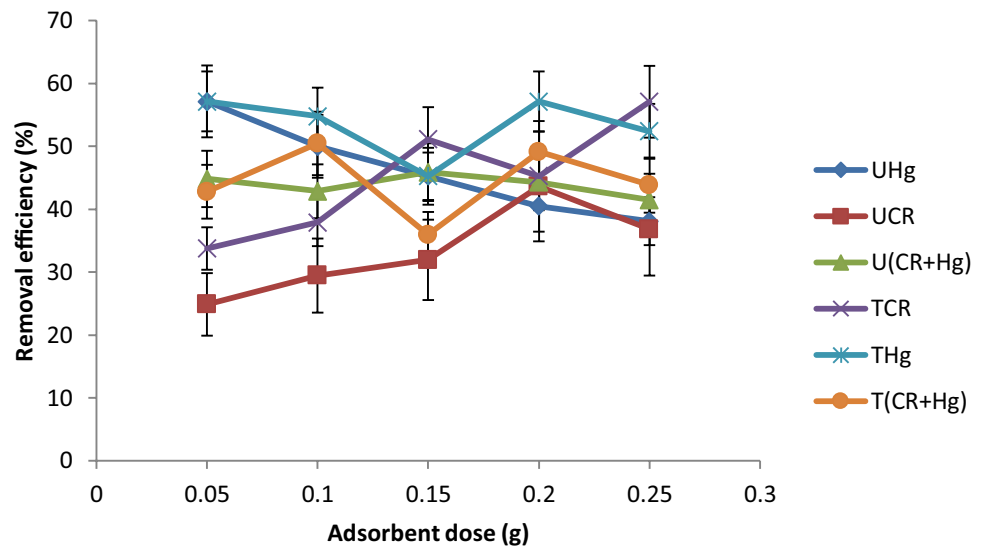
removal efficiency of Hg^{2+} tends to decrease from 95.48% to 91.67% and 50% to 40.48% for both UMLP and TMLP, respectively. On average, the removal efficiency of (Hg^{2+} and CR) binary mixture decrease from 55.17% to 52.78% and 63.82% to 52.81% for UMLP and TMLP, respectively. It was found that optimal contact times for both UMLP and TMLP are 62.5% at 90 min and 63.82% at 30 min, respectively. It was observed that UMLP has more negatively charged ions that compete with the anionic ion of the CR dye which brought about reduction in the removal efficiency and these ions are readily available to adsorb Hg^{2+} from the binary mixture. As the contact time increases, CR anionic dye tends to react with Hg^{2+} to get adsorbed at high percentage and also H^+ competes with Hg^{2+} which reduces the removal efficiency of Hg^{2+} in the binary solution. Using TMLP, K^+ tends to react with the anionic dye which caused CR dye to be removed at high percentage while K^+ competed with Hg^{2+} in the binary solution and the removal efficiency of Hg^{2+} was found to be low because K^+ is highly electropositive than Hg^{2+} . As the contact time increases, the persulphate anion competes with CR dye in the binary solution which brought about decrease in the removal efficiency of CR dye.

By comparing the binary mixture adsorption by various adsorbents, it was observed that TMLP has the relative maximum removal efficiency (63.82%) at contact time 30 min. Therefore, in the subsequent work, experiments were carried out at fixed optimum contact time of 30 min.

Effect of adsorbent dosage

The effect of adsorbent dosage on biosorption efficiency for Hg^{2+} , CR dye and their binary mixture were investigated. As

Fig. 5 Effect of adsorbent dosage on removal efficiency (%) of CR dye, Hg^{2+} and (Hg^{2+} and CR) binary solution



shown in Fig. 5, the maximum Hg^{2+} uptake was found to be 57.14% for both biomasses. The uptake capacities decreased at higher dosages which may be due to partial aggregation that occurs, resulting in decrease in the number of active sites on the surface of biomasses and can also be caused by overlapping of the negatively charged ions at the surface of the adsorbents (Gupta and Bhattacharyya 2008). However, at 0.20 g of TMLP, there was an increase in the removal of Hg^{2+} due to the availability of the active sites on the adsorbent and later the binding sites became exhausted.

The percentage removal of CR dye increase in adsorbent dosage of the adsorbent biomasses. This was as a result of increase in the number of active sites on the adsorbents' surfaces with respect to adsorbent dosages. For UMLP biomass, it was observed at dosage of 0.25 g, that the adsorption sites became aggregated which limited the availability of all the active sites and brought about the reduction in the percentage removal of CR dye. For TMLP biomass, the adsorbent dosage of 0.20 g tends to bring about reduction in the percentage removal of CR dye which was due to the non availability of all the active sites for CR dye adsorption and adsorbent dosage of 0.25 g, the percentage removal increased as a result of more active sites available to bind with the CR dye in the aqueous solution.

However, for the binary solution (Hg^{2+} and CR), the removal efficiency of Hg^{2+} decreased as the adsorbent dosages increased from 0.05 g to 2.50 g, whereas the removal efficiency of CR dye increased as the adsorbent dosages increased in the same range. On average, the removal efficiency of the binary mixture using UMLP decreases from 0.05 g (44.8%) to 0.1 g (42.85%), then increases and reaches the optimum adsorbent dosage at 0.15 g (45.89%) and gradually decrease to 41.49% at 0.25 g, whereas the removal efficiency of the binary mixture using TMLP increases from 0.05 g (42.78%) to 0.1 g (50.46%) the optimum adsorbent

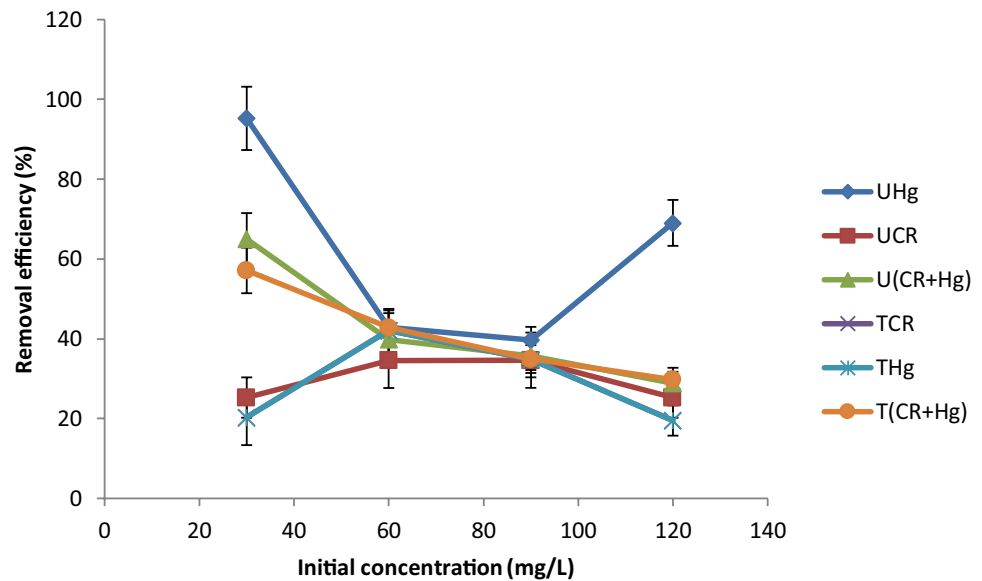
dosage and the last three adsorbent dosages removed 35.96%, 49.11% and 43.83%, respectively. At lower adsorbent dosage, there was more overlapping of the positively charged ions than the negatively charged ions and at higher adsorbent dosage, there is more overlapping of the negatively charged ions than the positively charged ions. The presence of potassium persulphate tends to increase the removal efficiency of the binary mixture such that at lower adsorbent dosage, persulphate anions reduce the strength of the overlapping of positively charged ions and vice versa.

Effect of initial concentration

The effect of initial concentration of Hg^{2+} , CR dye and (Hg^{2+} and CR dye) binary solution in the range of 30–120 mg/L on adsorption is shown in Fig. 6. The percentage removal of CR dye using UMLP increased from 30 mg/L (25.28%) to 90 mg/L (34.63%) and decreased to 25.28% for 120 mg/L while for TMLP, it increased from 30 mg/L (20.28%) to 60 mg/L (42.08%) and decreased gradually to 19.51% at 120 mg/L. It can be deduced that at low concentrations there could be unoccupied active sites on the adsorbent surface. Above optimal CR dye concentration, adsorption affinity of the adsorbent will gradually decrease with increasing CR dye concentration probably due to over saturation of the active sites. This retards the overall adsorption by these adsorbents. Similar work by Pathania and Singh (2017) supported this assertion.

Notably, the removal of Hg^{2+} was dependent on its concentration. As the initial concentration is increased the amount removed up to 50 mg/L for mercury and decreases at higher concentration. It was found that at low Hg^{2+} concentration biosorption rate increased which was probably due to the availability of biosorbent sites that take up the available Hg^{2+} more easily. However, at high

Fig. 6 Effect of initial concentration on removal efficiency (%) of CR dye, Hg^{2+} and (Hg^{2+} and CR) binary solution



concentration, the Hg^{2+} removal rate decreased which was caused by the saturation of some adsorption sites (Ashraf et al. 2010).

The removal efficiency of (Hg^{2+} and CR) binary mixture using UMLP and TMLP decreased as the initial concentration increased from 30 mg/L to 120 mg/L. This can be deduced that there are more available active sites at low concentration but as the binary solution's concentration increases, the active sites became filled up prior to the desorption process, and began to desorb.

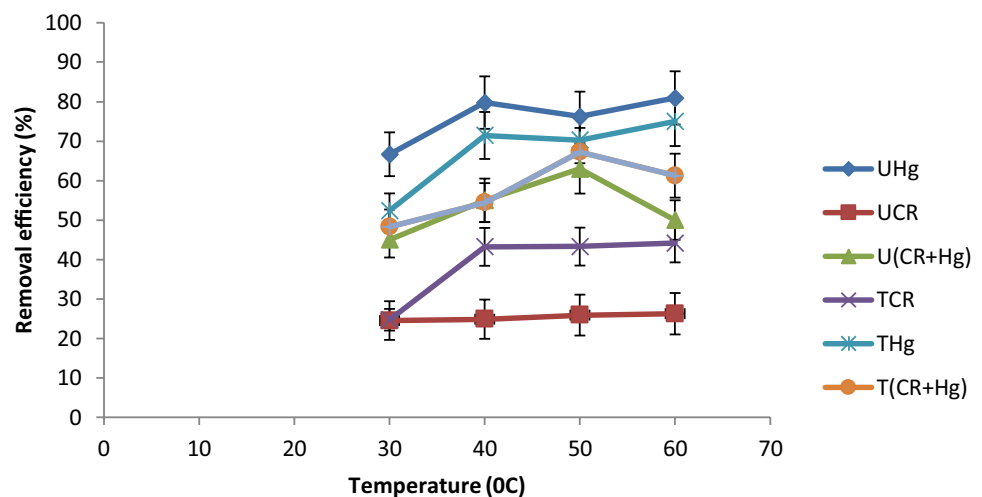
By comparing the binary mixture adsorption by various initial concentrations, it was observed that TMLP has the highest adsorption capacity q_e , which is best parameter for adsorption isotherm. Therefore, in the subsequent work, experiments were carried out at a fixed optimum adsorption capacity q_e of the initial concentration of 120 mg/L.

Effect of temperature on biosorbent removal efficiency

Figure 7 showed the effect of temperature on Hg^{2+} , CR dye and (Hg^{2+} and CR) binary solution uptake capacities of UMLP and TMLP at a temperature range 303–333 K. Optimum removal capacity of Hg^{2+} was obtained at 313 K for both types of biosorbents. The increase in the Hg^{2+} uptake capacity by both biosorbents was due to an enhanced rate of intra-particle diffusion of Hg^{2+} into the pores of the adsorbents. Beyond 40 °C, the increase in temperature leads to decrease in Hg^{2+} uptake which was due to the increase in the retarding forces acting on the diffusing ions. The adsorption of Hg^{2+} onto the surface of UMLP is higher than TMLP.

It was observed that as temperature increases, the percentage removal of CR dye increases for both biosorbents which was attributed to an increase in the mobility of the

Fig. 7 Effect of temperature on removal efficiency (%) of CR dye, Hg^{2+} and (Hg^{2+} and CR) binary solution



large dye ions and penetration into the biosorbent’s surface as the result of the enlargement of pore size of the adsorbents (Liu and Liu 2008). The optimal temperatures of both UMLP and TMLP are 40 °C and 50 °C, respectively. Beyond these optimal temperatures, the uptake capacity begins to drop, due to the increase in swelling effect that hinders the penetration of the large dye molecule into the surface of the adsorbents.

For the binary mixture using each adsorbent biomass, it was observed that as the temperature increased the removal efficiency of the binary mixture increased due to the increase in mobility of the binary solution which were penetrated into the adsorbent’s surface. At a temperature of 323 K, UMLP and TMLP adsorbed at their optimal temperatures at removal efficiencies of 63.42% and 67.23%, respectively. As the temperature increases from 323 K, the removal efficiency decreases to 48.67% and 61.25% for UMLP and TMLP, respectively. This decrease in removal efficiency with increase in temperature was as the result of drop in the removal efficiency of CR dye in the binary solution which can be attributed to CR dye solubility, i.e., the interaction between the solute and the solvent is stronger than that between the solute and the adsorbent.

Adsorption Isotherm

Adsorption isotherm provides the adsorption equilibria which are the fundamental physiochemical data for evaluating the applicability of the adsorption process as a unit operation. In this present work, the equilibrium data were analyzed using Langmuir (1916), Freundlich (1906) and Brunauer–Emette–Teller (Brunauer 1938) isotherm model.

These models were applied to describe the relationship between Hg²⁺, CR dye and (Hg²⁺ and CR) binary mixture concentration in their respective aqueous solution and that

on each adsorbent’s surface and the results are depicted in Table 1.

It is evident from the values of correlation coefficient *R*² in the Table 1 that the Langmuir isotherms model is efficient in describing the adsorption of (Hg²⁺ and CR) binary mixture onto UMLP and TMLP, Freundlich isotherm model is efficient in describing the adsorption of a single solute system, i.e., CR dye onto both adsorbents (UMLP and TMLP), and Hg²⁺ ions onto TMLP. Finally, BET model is efficient in describing the adsorption of CR dye onto TMLP because the adsorbate molecules adsorbed in more than one layer thickness on the surface of adsorbent.

The magnitude of *q_m*, the Langmuir constant indicated that the amount of (Hg²⁺ and CR) binary mixture per unit weight of each adsorbent to form complete monolayer on the surface was significantly high and the Freundlich isotherm constant, *n*, was found to be greater than 1 indicating that the adsorption of Hg²⁺, CR dye by UMLP and TMLP obeyed physisorption processes.

By comparing the results obtained it can be seen that *q_m* of Hg²⁺ by UMLP and TMLP are 23.70 mg/g and 29.41 mg/g, respectively, which implies that TMLP formed more monolayer with Hg²⁺ than UMLP. The magnitude of *q_m* of the adsorption of CR by UMLP is higher than TMLP, but *n*-value of the adsorption of CR dye by TMLP was higher than UMLP which implies that UMLP adhered more to monolayer adsorption process with CR dye than TMLP while TMLP adhered more to multi-layer adsorption pattern with CR dye than UMLP. The magnitude of *q_m* of the adsorption of (Hg²⁺ and CR) binary mixture by TMLP was higher than UMLP, but *n*-value of the adsorption of (Hg²⁺ and CR) binary mixture by UMLP was higher than TMLP which implies that TMLP formed more chemisorption process with (Hg²⁺ and CR) binary mixture than UMLP while

Table 1 Table of estimated values of constants of isotherms

| Isotherm parameters | UMLP | | | TMLP | | |
|-------------------------------|------------------|----------|-------------------------|------------------|--------|-------------------------|
| | Hg ²⁺ | CR | (Hg ²⁺ + CR) | Hg ²⁺ | CR | (Hg ²⁺ + CR) |
| Langmuir | | | | | | |
| <i>q_m</i> (mg/g) | 23.70 | 23.09 | 20.10 | 29.41 | 21.28 | 23.81 |
| <i>K_L</i> (L/mg) | 0.0256 | 0.0242 | 0.0609 | 0.075 | 0.019 | 0.07 |
| <i>R</i> ² | 0.7619 | 0.921 | 0.9662 | 0.994 | 0.9732 | 0.9989 |
| <i>R_L</i> | 0.6309 | 0.3552 | 0.1796 | 0.1509 | 0.4124 | 0.16 |
| Freundlich | | | | | | |
| <i>n</i> | 2.04 | 1.00 | 3.56 | 2.89 | 1.724 | 2.976 |
| <i>K_F</i> (mg/g) | 1.9024 | 1.4229 | 1.9024 | 5.34 | 1.026 | 4.764 |
| <i>R</i> ² | 0.863 | 0.9265 | 0.9224 | 0.9982 | 0.9458 | 0.9881 |
| Brunauer–Emmett–Teller | | | | | | |
| <i>q_m</i> (mg/g) | 0.0046 | 0.0107 | 0.0046 | 0.0096 | 0.015 | 0.047 |
| <i>K_B</i> | − 3.148 | − 0.9109 | − 2.107 | − 0.66 | − 3.45 | − 2.287 |
| <i>R</i> ² | 0.8398 | 0.9258 | 0.8515 | 0.9359 | 0.9871 | 0.9448 |

UMLP TMLP adhered more to physisorption process with (Hg^{2+} and CR) binary mixture than TMLP.

Adsorption kinetics

The kinetics data obtained from adsorption of Hg^{2+} , CR and (Hg^{2+} and CR) binary mixture onto both raw mango leaves powder (UMLP) and treated mango leaves powder (TMLP) were studied using two kinetic models, which are the pseudo-first-order kinetic (Eq. 1), pseudo-second-order kinetic (Eq. 2).

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t, \quad (2)$$

$$h = k_2 q_e^2, \quad (3)$$

where q_e is the amount of solute adsorbed at equilibrium (mg/g), q_t is the amount of solute adsorbed at time t (mg/g), k_1 pseudo-first-order rate constant (min^{-1}), h is the initial sorption rate (mg/g min) and k_2 is pseudo second-order rate constant (g/mg min). $\ln(q_e - q_t)$ against t gives calculated q_e and k_1 values while t/q_t against t gives the values of k_2 , h and calculated q_e which are given in Table 2.

These kinetic models were applied to investigate the reaction pathways and potential rate determining steps of the adsorption of Hg^{2+} , CR dye and (Hg^{2+} and CR) binary mixture onto UMLP and TMLP.

The best fit model was selected based on the linear regression correlation coefficient (R^2), which is a measure of how well the predicted values from a forecast model match with the experimental data.

The marked variation in the theoretical and experimental equilibrium adsorption capacity q_e values obtained for the pseudo-first-order model with low R^2 values suggested that the model was inadequate for describing the adsorption kinetics.

For pseudo-second-order model, the kinetic data showed excellent linearity with $R^2 > 0.9$, which made the calculated q_e and the experimental q_e values to be in good terms. This can be deduced that pseudo-second-order is well fitted for describing the adsorption of Hg^{2+} , CR dye and their binary mixture onto UMLP and TMLP supporting chemisorption process (Sharma and Nnadi 2013). Adsorption of CR dye on UMLP supported pseudo-first-order model because of its high R^2 value compared to that of pseudo-second-order.

Thermodynamic study

The thermodynamic parameters are determined using the following equation:

$$-\Delta G^\circ = RT \ln K_o, \quad (4)$$

where K_o , the distribution coefficient of the adsorbent is equal to q_e/C_e , $T(K)$ is the solution temperature and R is the universal gas constant which is 8.314 J/mol K. Table 3 summarized the values of the thermodynamic quantities obtained from the Van't Hoff equation. Entropy change of adsorption of Hg^{2+} , CR dye and their binary mixture, ΔS_{ad} which measured degree of randomness was found to be positive for Hg^{2+} onto UMLP, CR dye onto TMLP and (Hg^{2+} and CR) binary solution onto both adsorbents indicating decrease in entropy and it was found to be negative for Hg^{2+} onto TMLP and CR dye onto UMLP. The positive entropy change obtained indicated that the association of the adsorbate at the solid–solution interface becomes more random; the existence of the molecules in solution is less random than that on surface (Yu et al. 2004) while the negative values of entropy change showed that no significant change occurred in the internal structure of the active site of the adsorbents.

The positive values of enthalpy change of adsorption for Hg^{2+} , CR dye and their binary mixture confirmed the endothermic nature of adsorption process.

Gibbs free energy, ΔG is important parameter for spontaneity of adsorption process. In this study, the

Table 2 Comparison of kinetic parameters for the adsorption of Hg^{2+} , CR dye and their binary mixture onto UMLP and TMLP at pH 7

| Kinetic model and parameters | UMLP | | | TMLP | | |
|------------------------------|------------------|---------|--------------------------|------------------|---------|--------------------------|
| | Hg^{2+} | CR | (Hg^{2+} + CR) | Hg^{2+} | CR | (Hg^{2+} + CR) |
| q_{exp} (mg/g) | 55.6 | 25.1 | 46.45 | 51.9 | 31.79 | 33.55 |
| Pseudo-first order | | | | | | |
| q_{cal} (mg/g) | 22.04 | 20.11 | 0.0682 | 4.586 | 21.52 | 1.297 |
| K_1 (min^{-1}) | 0.036 | 0.021 | -0.169 | -0.02 | 0.056 | 0.036 |
| R^2 RMSE | 0.9820 | 0.884 | 0.768 | 0.277 | 0.695 | 0.017 |
| Pseudo-second order | | | | | | |
| q_{cal} (mg/g) | 55.56 | 22.22 | 35.71 | 45.46 | 34.48 | 31.25 |
| k_2 (g/mg min) | 0.00498 | 0.00282 | 0.00945 | 0.0167 | 0.00389 | 0.0683 |
| h (mg/g min) | 15.384 | 1.391 | 12.048 | 34.483 | 4.630 | 66.67 |
| R^2 RMSE | 0.999 | 0.844 | 0.984 | 0.983 | 0.923 | 0.920 |

Table 3 Thermodynamic parameters for the adsorption of Hg²⁺, CR dye and their binary mixture onto UMLP and TMLP at different temperatures

| Temperature (K) | Hg ²⁺ – UMLP system | | | Hg ²⁺ – TMLP system | | |
|-----------------|--|------------------------|--------------------------|---|------------------------|--------------------------|
| | ΔG (KJ/mol) | ΔH (KJ/mol) | ΔS (J/mol. K) | ΔG (KJ/mol) | ΔH (KJ/mol) | ΔS (J/mol. K) |
| 303 | 0 | 17.42 | 58.81 | 1.506 | 25.06 | – 79.32 |
| 313 | – 1.77 | | | – 0.58 | | |
| 323 | – 1.26 | | | – 0.45 | | |
| 333 | – 2.09 | | | – 1.12 | | |
| | CR – UMLP system | | | CR – TMLP system | | |
| | ΔG (KJ/mol) | ΔH (KJ/mol) | ΔS (J/mol. K) | ΔG (KJ/mol) | ΔH (KJ/mol) | ΔS (J/mol. K) |
| 303 | 4.58 | 2.77 | – 6.01 | 4.55 | 21.865 | 59.10 |
| 313 | 4.68 | | | 2.52 | | |
| 323 | 4.69 | | | 2.59 | | |
| 333 | 4.78 | | | 2.57 | | |
| | (Hg ²⁺ and CR)s – UMLP system | | | (Hg ²⁺ and CR) – TMLP system | | |
| | ΔG (KJ/mol) | ΔH (KJ/mol) | ΔS (J/mol. K) | ΔG (KJ/mol) | ΔH (KJ/mol) | ΔS (J/mol. K) |
| 303 | 2.13 | 16.15 | 47.31 | 1.92 | 25.71 | 78.50 |
| 313 | 1.03 | | | 1.35 | | |
| 323 | 0.52 | | | – 0.07 | | |
| 333 | 0.77 | | | – 0.21 | | |

spontaneity of adsorption process, ΔG_{ads} of Hg²⁺ onto UMLP was found to range from 0 kJ/mol to –2.086 kJ/mol while onto TMLP was found to range from +1.506 kJ/mol to –1.123 kJ/mol. It suggested that the adsorption of Hg²⁺ onto UMLP and TMLP was spontaneous and their adsorption processes are physisorption. ΔG_{ads} of CR dye onto UMLP and TMLP were found to be positive throughout the working temperatures which indicate that the adsorption processes are non-spontaneous. These findings agreed with other researchers' work in support of the non-spontaneity due to the positive G_{ads} values (Ozean and Ozean 2005).

ΔG_{ads} of the binary mixture onto UMLP was found to be positive throughout the temperatures while onto TMLP, ranges from +1.920 kJ/mol to – 0.2085 kJ/mol which suggested that ΔG_{ads} of the binary mixture on UMLP is non-spontaneous and (Hg²⁺ and CR) binary mixture–TMLP system showed spontaneous/feasible reaction at higher temperature. (Hg²⁺ and CR) binary mixture–UMLP system could be spontaneous at higher temperature since the ΔG_{ads} data presented in Table 3 showed decrease in the values.

Conclusion

The present study has shown the effectiveness of the raw and treated mango leaves powder on removal of Hg²⁺, CR dye and their binary mixture from the aqueous solution.

Effects of the different experimental parameters of the adsorption process that influenced the efficiencies of the adsorbents have been evaluated and optimized at pH 7, contact time of 30 min, adsorbent dosage of 0.1 g, initial concentration of 120 mg/L and at temperature of 50 °C. This study showed that the removal of binary mixture (BM) was efficient with the Langmuir isotherm model while the removal of single pollutant was efficient with both Freundlich and BET isotherm models. Kinetic data were best fit to pseudo-second-order model except the adsorption of CR dye on UMLP that agreed with pseudo-first-order. Thermodynamic studies predict that the adsorptions of BM on TMLP and of Hg²⁺ on both adsorbents are feasible, spontaneous and endothermic in nature while the adsorption of BM on UMLP and of CR dye on both adsorbents are non-spontaneous and endothermic in nature.

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