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2^k Optimization approach for the removal of Pb^{2+} ions from water contaminated from oil-well drilling point on to MWCNTs

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Abstract

The release of Pb^{2+} into the surrounding ecosystem has adverse effects on man and animal, hence, removing such harmful heavy metal from water system calls for urgent attention. The potential application of Multi -walled carbon nanotubes, MWCNTs, towards the lead (II) ions removal from oil polluted water body was studied and optimized via 2^k factorial experimental approach. The MWCNTs produced was characterized via High Resolution Transmission Electron Microscope (HR-TEM), High Resolution Scanning Electron microscope (HR-SEM), Thermogravimetric Analysis (TGA), Fourier Transform Infrared (FTIR) and Brenuer-Emmette-Teller (BET) to determine the internal morphology, surface morphology, thermal stability, functional group and surface area respectively. The results of the HR-TEM depict the nano-structural diameter of the produced MWCNTs with continuous strands of tubes as depicted by SEM micrograph. The MWCNTs surface area produced was obtained to be 540 m^2/g. The sorption of Pb^{2+} ions was optimized using 2k design approach where speed (rpm), absorbent dosage (g), temperature (^oC) and time (min) were studied in a batch condition. The optimum conditions that give maximum sorption of Pb^{2+} ions on to the surfaces and the pores of the developed MWCNTs adsorbent were obtained at 60 min contact time, 59.89 ^oC, 0.20 g of adsorbent dosage and 599.98 rpm of agitation. Thus, the highest percentage sorption of Pb^{2+} ions by the MWCNTs from the oil-polluted water body was 99.5%. Hence, this study has demonstrated the potentials of MWCNTs as an effective and efficient sorbent for Pb^{2+} sorption from oil polluted wastewater.

IOP Conf. Series: Materials Science and Engineering **805** (2020) 012013 doi:10.1088/1757-899X/805/1/012013

1. Introduction

Several pollutants from non-point and point sources have contributed significantly to contamination of drinking and groundwater [1] and amongst commonly observed contaminants; inorganic lead pollutants stand second on profile of most hazardous metals with significant health risks for the living beings. These beings and by extension water bodies are possibly exposed to lead in various forms to include pipe corrosion, faucets, household plumbing systems, old paints, mining, smelting, battery manufacturing, and other industrial and urban wastes [2-4]. Wastewater discharges from mining, metallurgical, tannery, battery, chemical and plastics manufacturing industries have contributed immensely to the quantity of lead (II) ions in water bodies whose concentration has raised a huge concern [5]. The types of emerging pollutants are also increasing while the challenges posed by traditional pollutants are not efficiently solved yet.

Generally, toxic metal-polluted waters and particularly accumulation of lead, cause several disease problems such as damage to the central nervous induced damages, renal kidney disease, mental retardation, cancer and anemia including cardiovascular disorders [6-7]. Removal of toxic metals has been identified as one of the major challenges in ensuring safe water for all in addition to protecting the environment [8-9]. It is important to note that there exist different conventional processes used as purification techniques but most offer some disadvantages [3]. Among the conventional and most commonly employed means of water purification is the application of carbon nanotubes; MWCNTs as novel sorbents in an adsorption process.

MWCNTs are identified to possess excellent properties; physical, chemical, mechanical and electrical, which lead to great potential application in various fields to include adsorption in water purification. The large specific surface area (SSA) and the appreciable chemical and thermal stability of MWCNTs associated to their easy large-scale synthesis make them good candidates for adsorption kinetics study [10]. MWCNTs possess high sorption capacity compared to the activated carbon (AC) during a sorption process. The observed high sorption capacity exhibited by MWCNTs is as a result of strong interaction between MWCNTs and sorbates which exist on the surfaces of the adsorbent during the sorption process [11], dioxin for example. MWCNTs have an abundant potential application of removing pollutants like lead (Pb) ions, copper (Cu) ions from water bodies [12-13].

IOP Conf. Series: Materials Science and Engineering **805** (2020) 012013 doi:10.1088/1757-899X/805/1/012013

Sorption process is categorized as surface phenomenon where sorbate molecules adhere to the sorbent surface. The size of sorbent molecules that interact ranges from microns to nanometer. The nanomaterials (<100 nm) possess larger surface for sorption and thereby provides better sorption efficiency compared to bulk sorbents. The process of separation using the nanosized adsorbents is termed as nano-adsorption. Nanoparticles are applied individually or in the form of composites and more obviously, the application of nanocomposites give high sorption efficiencies owing to the presence of simultaneously acting adsorption mechanism; physical and chemical sorption mechanisms [14]. Specifically for precise occasion of sorption of lead, the principal mechanisms govern the sorption process are ranging from ion exchange, complexation, chemisorption, electrostatic interaction and mono-ion layer physical adsorption [15-17].

Several adsorbents such as activated carbon, alumina, silica, zeolites, titania have been extensively applied for the sorption of pollutants from wastewater. The application of MWCNTs as sorbent has attracted appreciable interest due to its ability to be functionalized as a result of defects walls which aid to achieving any intended objectives. The controlling mechanism is characteristically dependent on the nature of the nanosorbent used and the conditions of operation [14]. It has been established that various factors which include pH, pH*zpc*, adsorbent dose, size and shape were found responsible for causing changes in adsorption efficiency.

This study focuses on the production of MWCNTs in a CVD reactor and optimization of adsorptive process parameter for Pb^{2+} ions removal of pollutants from a contaminated water body with Fe-Co/kaolin MWCNTs as adsorbents using 2^k factorial design of experimental.

2. Materials and Methods

All the chemicals used in the work were of analytical grade with very high percentage purity of 95-99.99%, and they were used without any prior purification. The characteristics properties of catalyst used in this research work have been presented elsewhere [18].

2.1 MWCNTs Synthesis

The MWCNTs used was produced in a catalytic vapour deposition (CVD) reactor. Exactly 1.0 g of the sourced catalyst was measured in a crucible and placed in the center of the CVD reactor. The CVD was purged using N_2 at a flow rate of 50 ml/min at constant heating rate. Immediately the temperature reached 700 ^oC, the reactant's flow, acetylene was released to the reactor at 100 ml/min while the nitrogen flow was increased to 100 ml/min to serve as carrier gas for a reaction time of 45 min. The flow of nitrogen gas was then reduced to 50 ml/min at the completion of the reaction time and the acetylene flow was then stopped. The equipment was allowed to cool after which the produced nanomaterial was removed and kept for further analysis.

2.2 Wastewater collection and analysis

The contaminated water sample was collected from 5 different points into separate polythene bottles from a water body situated behind an oil-well drilling point in Delta State. Exactly 5.0 cm^3 of concentrated nitric acid was added to the collected wastewater sample. Further, 10 cm^3 of the water sample was digested with 5 cm^3 of HNO_3 concentrated and 2 cm^3 of HCl (5:2). Then, 15 cm^3 of deionized water was added and filtered using Whatman paper No. 45. The final filtrate was made up to 50 cm^3 of the volumetric flask with deionized water. The filtrate was analyzed using atomic absorption spectrophotometer for initial concentration of Pb^{2+}.

2.3 Adsorption Process

The adsorption process was carried out via batch adsorption method designed using 2^k factorial whereby 16 different runs were obtained for the study. Wastewater (50 ml) was transferred into 100 ml beakers for each experimental batch following 2^k optimization design approach (Table 1) and placed in a water batch shaker at specified temperature and time. After the completion of the adsorption process, the aliquot obtained was centrifuged at 300 and 600 rpm for 60 min and then filtered using a filter unit into a sample bottle for spectrophotometric analysis. Adsorbent dosage, temperature, speed, and residence time affecting the process were studied using 2^k optimization design approach. The percentage sorption of Pb^{2+} was calculated using the equation as presented in equation 1:

$$\% R = \left(\frac{C_u - C_v}{C_u}\right) \times 100 \qquad (1)$$

Where Cu and Cv are the Pb^{2+} concentrations in grams per litre initially and at time, t respectively while %R denotes percentage sorption of Pb^{2+} ions from solution.

IOP Conf. Series: Materials Science and Engineering **805** (2020) 012013 doi:10.1088/1757-899X/805/1/012013

Table 1. Experimental factors and levels used in the factorial design

Independent variables	Coded symbol	Range and	Level
		-1	+1
Contact time (min)	A	0.1	0.2
Temperature (^{o}C)	B	30	60
Adsorbent dosage (g/l)	C	300	600
Speed (rpm)	D	30	60

3 Results and Discussion

3.1 Characterization of the as-produced MWCNTs

The internal morphology of the produced MWCNTs adsorbent as presented in Figure 1, which shows the nano-structure of the MWCNTs formed over the applied catalyst.

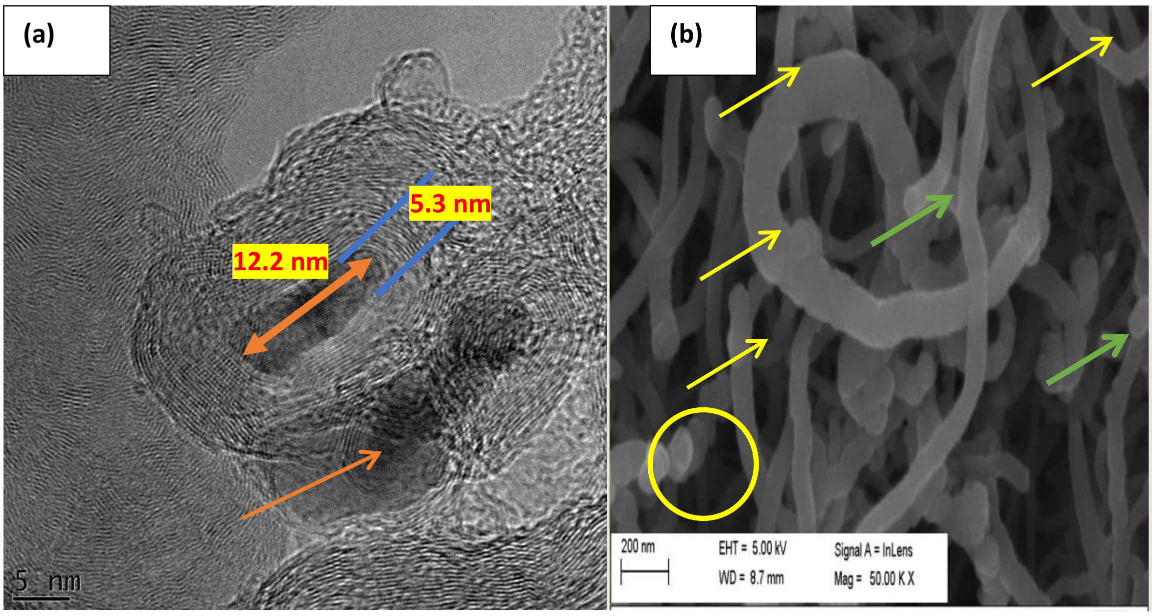

Figure 1. (a) TEM micrograph and (b) SEM micrograph for the developed MWCNTs

The internal morphology of the developed MWCNTs with unique diameter having several concentric tubes' walls was as depicted in Figure 1 (a). The produced MWCNTs have a tube dimension of 5.3 × 12.2 nm architecture confirming the nanoscale nature of the produced

IOP Conf. Series: Materials Science and Engineering **805** (2020) 012013 doi:10.1088/1757-899X/805/1/012013

material (Figure 1a). The surface morphologies of the MWCNTs produced comprise of the continuous strands of nanotubes with varied diameter as presented in Figure 1 (b) with yellow arrows. The reason for the observed MWCNTs of varied diameter could be as a result of the inherent varied particle sizes of the catalyst used during the MWCNTs production. It was also observed that the produced MWCNTs have numerous branch tubes which could be as a result of the synthesis condition employed.

The thermal analysis and the surface functional group of the developed MWCNTs were determined using TGA and FTIR respectively and the results are as shown in Figure 2(a-b).

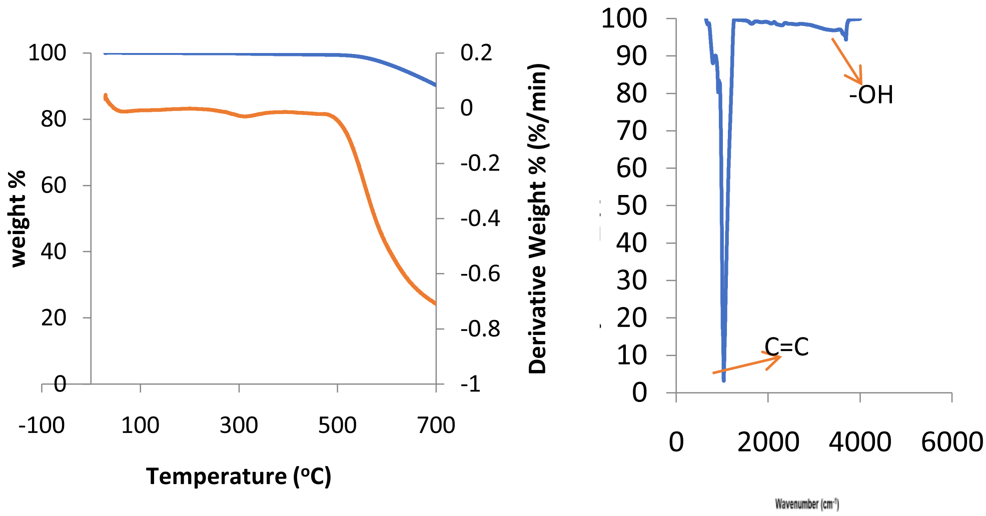

Figure 2. (a) TGA thermograph and (b) FTIR spectra of the developed MWCNTs

The result of the thermal stability as depicted in Figure 2a shows that the produced MWCNTs possess an improved thermal stability with onset degradation at 500.21 ^{o}C amounts to about 0.992 % weight loss from room temperature. The percentage degradation of the MWCNTs was also obtained to be 6.32 % between the temperature ranges of 29.67-700 ^{o}C. The obtained percentage weight loss in the MWCNTs weight could be linked to the presence of active parts of the catalyst used as well and the possible presence of amorphous formation during the MWCNTs nucleation process. Figure 2b shows the occurrence of –OH and C=C bound formation at the wavelength of 3700 and 1056 cm^{-1} respectively.

The surface area of the produced MWCNTs was also determined via BET technique and it was obtained to be 540 m^2/g. The obtained surface area is highly appreciable for effective adsorption process.

3.2 Optimization Studies for sorption of $Pb2^+$

The characterized MWCNTs were applied as sorbents for the sorption of Pb^{2+} from oil polluted water in a batch adsorption process via optimization approach. The effect of temperature, contact time, sorbent dosage and agitation were optimized via 2^k optimization approach as depicted in Table 2.

Table 2. Basic experimental runs obtained for the optimization study and parameters

Run No.	Contact time (min)	Temperature (^oC)	Dosage (g)	Speed (rpm)	% Pb Removal
1.	30	60	0.10	600	82.15
2.	30	30	0.10	600	78.32
3.	60	30	0.10	300	28.43
4.	30	60	0.10	300	39.16
5.	60	30	0.20	600	84.54
6.	60	60	0.10	600	44.58
7.	30	30	0.20	600	84.98
8.	60	30	0.20	300	74.94
9.	60	60	0.10	300	66.04
10.	60	30	0.10	600	60.29
11.	30	60	0.20	300	89.09
12.	30	60	0.20	600	96.72
13.	30	30	0.10	300	18.12
14.	30	30	0.20	300	69.49
15.	60	60	0.20	300	47.20
16.	60	60	0.20	600	99.50

Analysis of variance (ANOVA) was used for the estimation of the interacting factors and the main effects for sorption of Pb^{2+} (Table 3). The significance of the process parameters were quantified via the sum of squares, SS. It was observed that as the value of SS increases, the significance of the corresponding factor in the undergoing process also increased. The relating effects of each independent process factors were statistically significant at $P < 0.05$ [19]. The Pareto chart shows the number of factors that has significant effect on the sorption process. Hence, any bar that cuts the line indicates that such effects are significant. Therefore, only C and D are significant for the sorption of Pb^{2+} on to MWCNTs sorbent as presented in Figure 3.

Table 3. ANOVA for selected factorial model

Sources	Sum of squares	df	Mean square	F Value	P-Value Prob>F	Remark
Model	7067.96	4	1766.99	5.60	0.0104	significant
A-Contact Time	66.06	1	66.06	0.21	0.6563	
B-Temperature	128.43	1	128.43	0.41	0.5367	
C-Dosage	3886.59	1	3886.59	12.31	0.0049	
D-Speed	2986.90	1	2986.90	9.46	0.0106	
Residual	3472.99	11	315.73			
Cor Total	10540.96	15				

After discarding insignificant terms from the model generated, the resultant models can be expressed as:

Final Equation in Terms of Coded Factors:

$$\%\, removal = 65.22 - 2.03A + 2.83B + 15.59C + 13.66D$$

Final Equation in Terms of significant Coded Factors:

$$\%\, removal = 65.22 + 15.59C + 13.66D$$

Final Equation in Terms of Actual Factors:

IOP Conf. Series: Materials Science and Engineering **805** (2020) 012013 doi:10.1088/1757-899X/805/1/012013

$$\% \, removal = -24.92813 - 0.13546 \times contact\ time + 0.18887 \times temperature + 311.71250 \times dosage + 0.091088 \times speed$$

Final Equation in Terms of significant Actual Factors:

$$\% \, removal = -24.92813 + 311.71250 \times dosage + 0.091088 \times speed$$

The optimum points of the sorption process was determined via numerical analysis using desirability test. The optimum conditions give maximum sorption of Pb^{2+} on to the surfaces and the pores of the developed MWCNTs adsorbent were obtained at 60 min contact time, 59.89 ^{o}C temperature, 0.20 g of adsorbent dosage and 599.98 rpm of agitation speed. The above conditions led to the maximum desirability of 0.9899 as presented in Figure 4(a). The 3-D plots showing effects of parameters on adsorption of Pb^{2+} on to MWCNTs adsorbent are as shown in Figure 5.

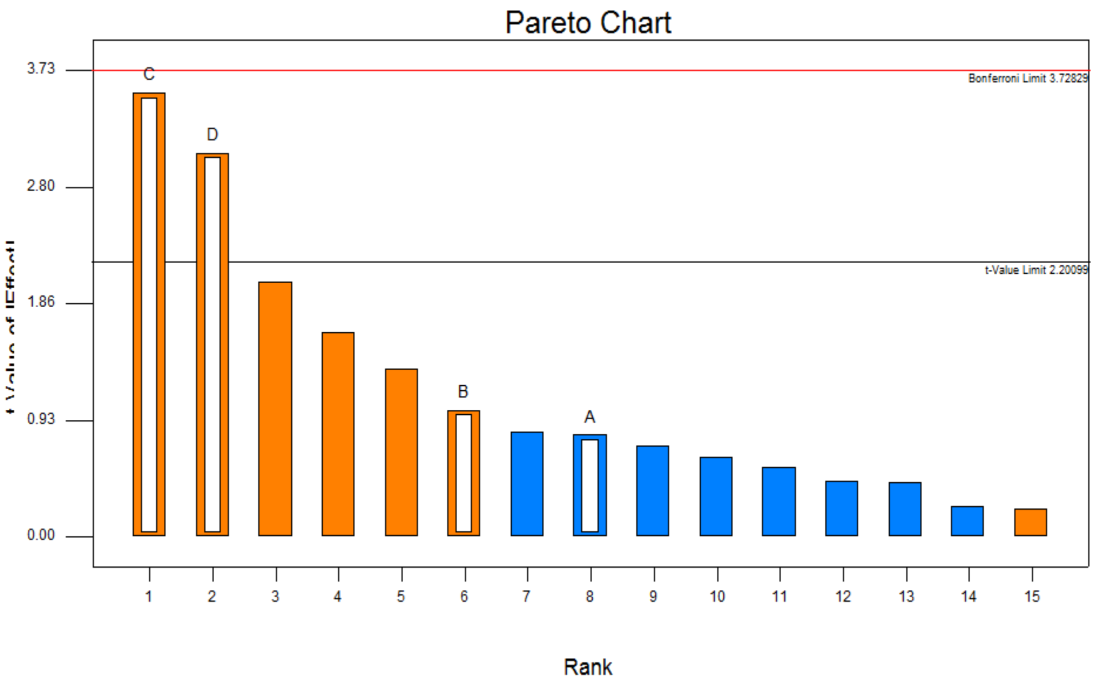

Figure 3. A Pareto chart showing the significant effect having effects on the sorption process

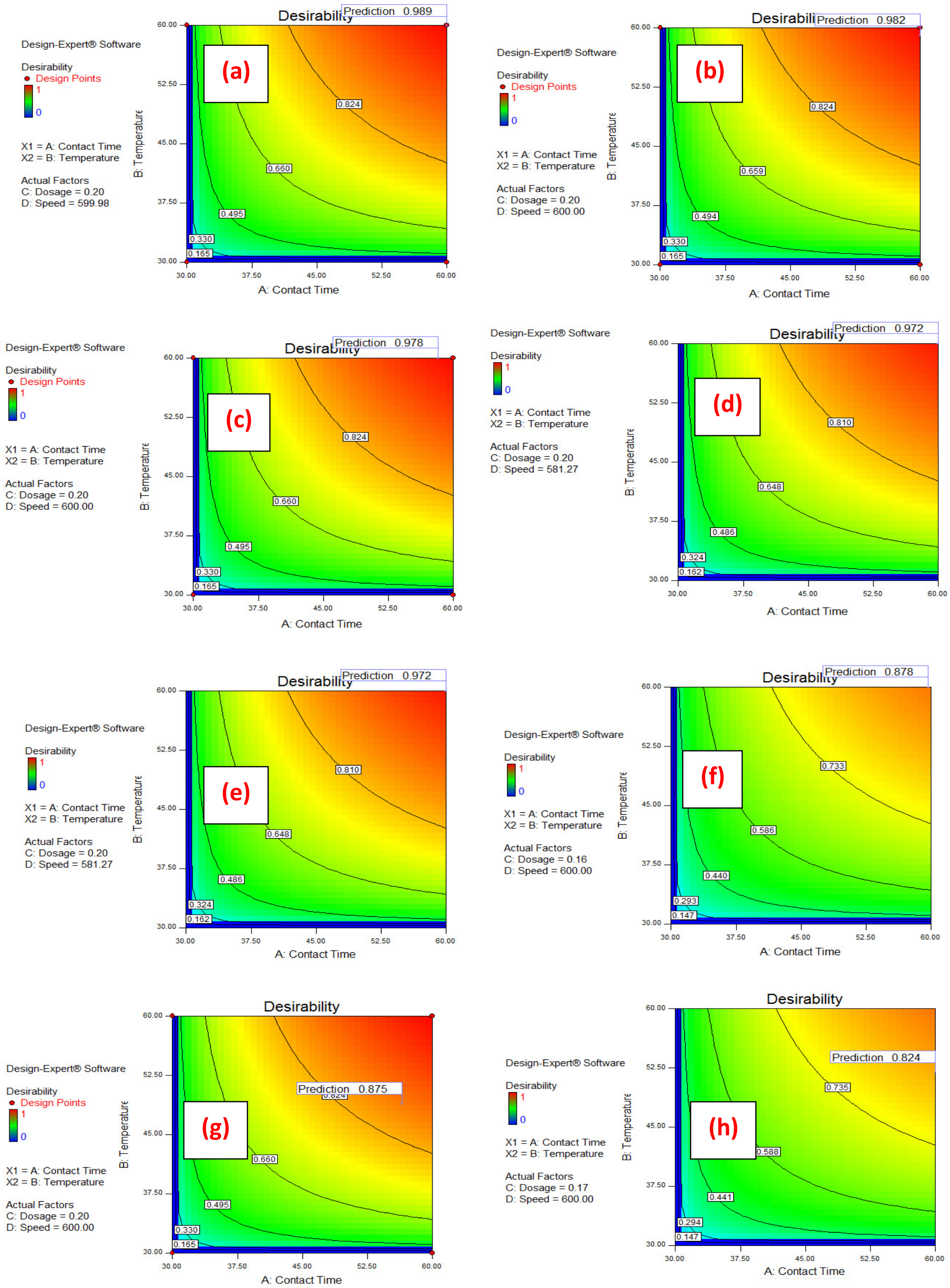

Figure 4. Desirabilty graphs for optimum condition determination

IOP Conf. Series: Materials Science and Engineering **805** (2020) 012013 doi:10.1088/1757-899X/805/1/012013

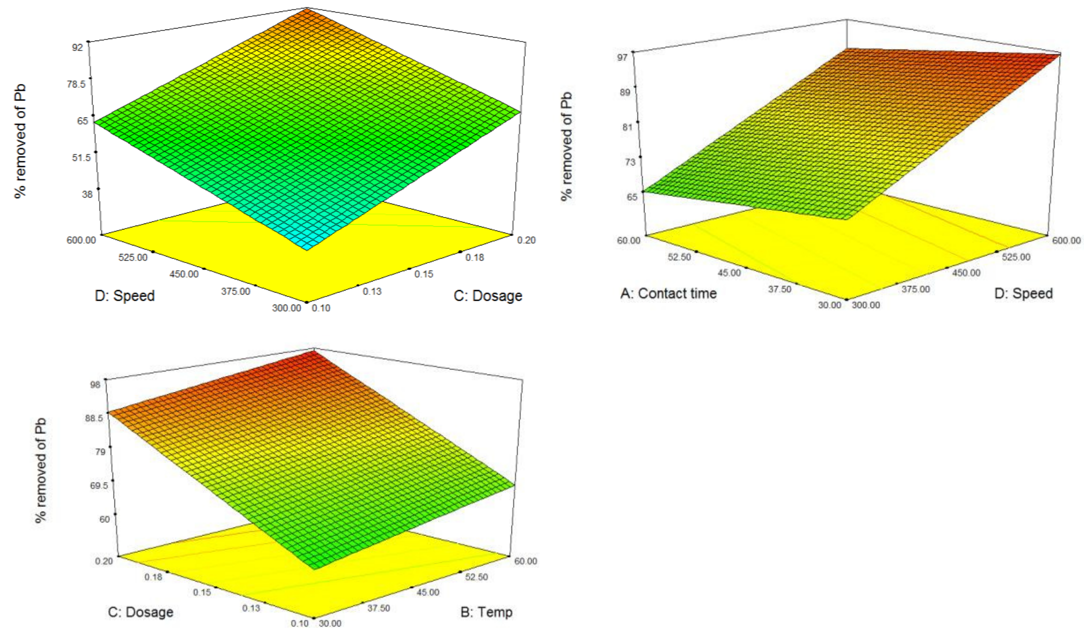

Figure 5. 3-D Plots showing effects of parameters on the lead adsorption on to MWCNTs adsorbent

4. Conclusion

Adsorption process as widely regarded as one of the effective and efficient heavy metal ions removal technology. The developed MWCNTs adsorbent possesses a diameter in the matrix of 5.3 × 12.2 nm with continuous strands of tubes as depicted by the TEM and SEM respectively. The MWCNTs adsorbent possesses a relatively large surface area of 540 m^2/g making it had the adsorptive potential towards the removal of impurities. The sorption of Pb^{2+} ions on the surface of the MWCNTs was optimized via 2^k factorial design. The optimum process that give maximum sorption of Pb^{2+} ions on to the surfaces and the pores of the developed MWCNTs adsorbent were obtained at 60 min contact time, 59.89 ^oC temperature, 0.20 g of adsorbent dosage and 599.98 rpm of agitation speed. Thus, this work on sorption of lead ions on Fe-Co/ Kaolin MWCNTs was successfully carried out for process optimization. The utilized MWCNTs were effective for Pb^{2+} ions sorption from oil-polluted water body.

References

[1] Ali I 2014 Water treatment by adsorption columns: evaluation at ground level. *Sep. Purif. Rev.* **43** (3) pp 175-205.

[2] Kumari M, Pittman CU and Mohan D 2015 Heavy metals [chromium (VI) and lead (II)] removal from water using mesoporous magnetite (Fe_3O_4) nanospheres. *J. Colloid Interf. Sci.* **442** pp 120-132.

[3] Mubarak N, Sahu J, Abdullah E and Jayakumar N 2014 Removal of heavy metals from wastewater using carbon nanotubes. *Sep. Purif. Rev.* **43** (4) pp 311-338.

[4] Salam MA 2013 Coating carbon nanotubes with crystalline manganese dioxide nanoparticles and their application for lead ions removal from model and real water. *Colloids Surf. A: Physichochem. Eng. Aspect* **419** pp 69-79.

[5] Kocabaş-Ataklı ZÖ and Yürüm Y 2013 Synthesis and characterization of anatase nanoadsorbent and application in removal of lead, copper and arsenic from water. *Chem. Eng. J.* **225** pp 625-635.

[6] Calderon J, Navarro ME, Jimenez-Capdeville ME, Santos-Diaz MA, Golden A, Rodriguez-Leyva I, Borja-Aburto V and Dıaz-Barriga F 2001 Exposure to arsenic and lead and neuropsychological development in Mexican children. *Environ. Res*. **85** (2) pp 69-76.

[7] Mortada W, Sobh M, El-Defrawy M and Farahat S (2001) Study of lead exposure from automobile exhaust as a risk for nephrotoxicity among traffic policemen. *Am. J. Nephrol.* **21** (4) pp 274-279.

[8] Bansal RC and Goyal M 2005 *Activated Carbon Adsorption*. *Taylor and Francis Group*, London, pp+ 351–353.

[9] Muyibi SA, Ambali AR and Eissa GS 2008 Development-induced water pollution in Malaysia: policy implication from an econometric analysis. *Water Policy* **10** (2) pp 193-206.

[10] Wang Y, Wei F, Luo G, Yu H and Gu G 2002 The large-scale production of carbon nanotubes in a nano-agglomerate fluidized-bed reactor. *Chem. Phys. Lett.* **364** (5-6) pp 568-572.

[11] Long QR and Yang RT 2001 Carbon nanotubes as superior sorbent for dioxin removal. *J. Am. Chem. Soc*. **123** (9) pp 2058-2059.

[12] Peng X, Luan Z, Di Z, Zhang Z and Zhu C 2005 Carbon nanotubes–iron oxides magnetic composites as adsorbent for removal of Pb(II) and Cu(II) from water. *Carbon* **43** pp 880-883.

[13] Li YH, Zhu Y, Zhao Y, Wu D and Luan Z 2006 Different morphologies of carbon nanotubes effect on the lead removal from aqueous solution. *Diam. Relat. Mater*. **15** (1) pp 9094.

[14] Bhatia M, Babu RS, Sonawane SH, Gogate PR, Girdhar A, Reddy ER and Pola M 2016 Application of nanoadsorbents for removal of lead from water. *Int. J. Environ. Sci. Technol*. **14** (5) pp 1135-1154.
[15] Zhan X-M, and Zhao X 2003 Mechanism of lead adsorption from aqueous solutions using an adsorbent synthesized from natural condensed tannin. *Water Res.* **37** (16) pp 3905-3912.
[16] Choi SB, and Yun Y-S 2006 Biosorption of cadmium by various types of dried sludge: an equilibrium study and investigation of mechanisms. *J. Hazard Mater.* **138** (2) pp 378-383.
[17] Yu B, Zhang Y, Shukla A, Shukla SS and Dorris KL 2001 The removal of heavy metals from aqueous solutions by sawdust adsorption—removal of lead and comparison of its adsorption with copper. *J. Hazard Mater.* **84** (1) pp 83-94.
[18] Kariim I, Abdulkareem AS, Abubakre OK, Mohammed IA, Bankole MT and Jimoh TO 2015 Studies on the suitability of alumina as bimetallic catalyst support for MWCNTs growth in a CVD reactor. *Int. Eng. Conf.* pp 296-305.
[19] Abdel-Ghani NT, Hegazy AK, El-Chaghaby GA and Lima EC 2009 Factorial experimental design for biosorption of iron and zinc using *Typha domingensis* phytomass. *Desalination* **249** (1) pp 343-347.