APPENDICES

APPENDIX A

Calibration curve and calculations

A.1 Calibration of copper from calibration curve

In order to determine the calibration curve of Cu^{2+} ion from copper nitrate solutions, the various concentrations of standard copper were prepared. The absorbance of Cu^{2+} ion from copper nitrate solutions was measured using atomic absorption spectrophotometer (AAS).

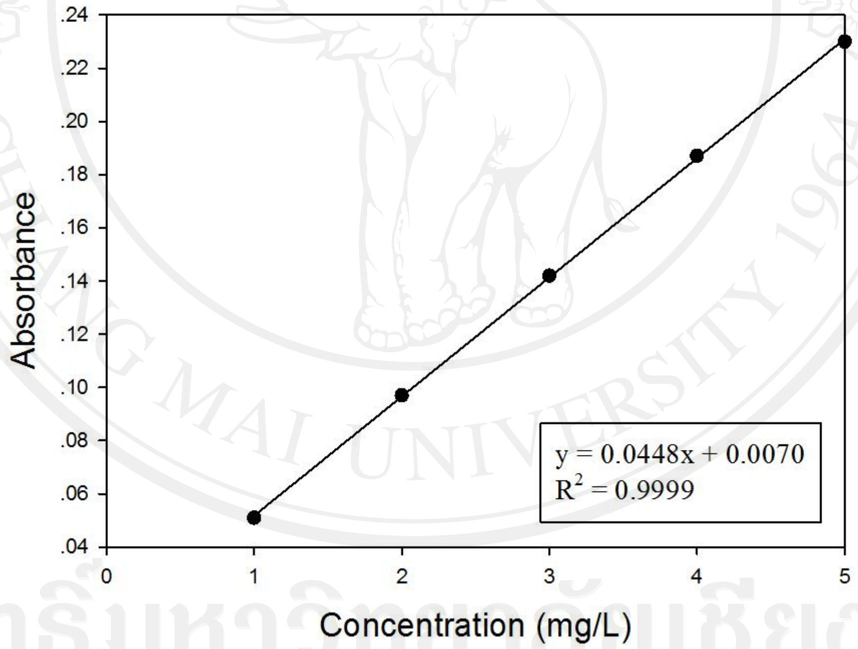

Figure A1 Calibration curve of copper

Equation of calibration curve: y = 0.0448x + 0.0070

When y = absorbance (ABS) and x = copper concentration

$$x = \frac{ABS - 0.0070}{0.0448}$$

A.2 Calibration of zinc from calibration curve

In order to determine the calibration curve of Zn^{2+} ion from zinc nitrate solutions, the various concentrations of standard zinc were prepared. The absorbance of Zn^{2+} ion from zinc nitrate solutions was measured using atomic absorption spectrophotometer (AAS).

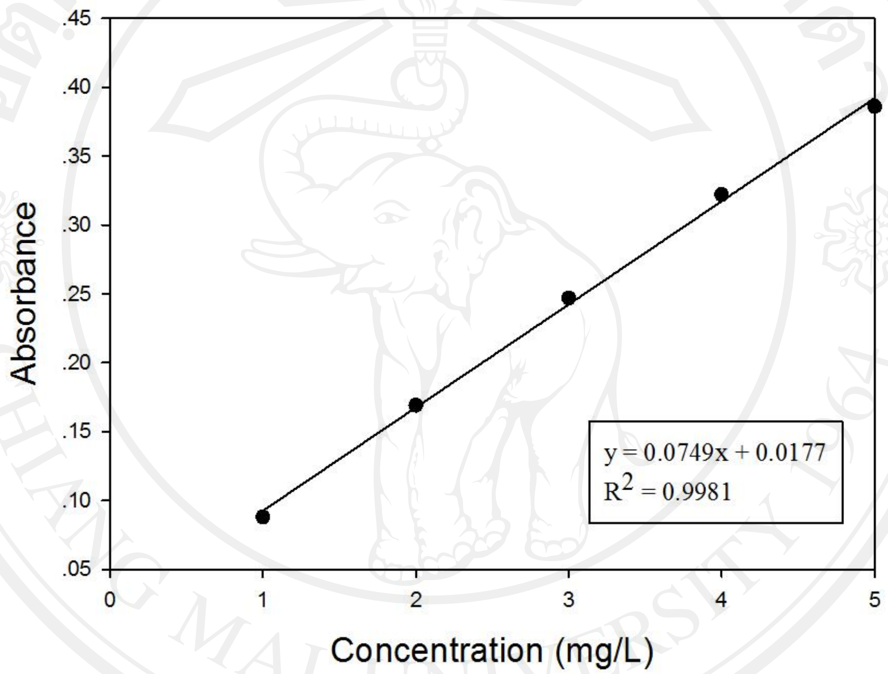

Figure A2 Calibration curve of zinc

Equation of calibration curve: y = 0.0749x + 0.0177

When y = absorbance (ABS) and x = zinc concentration

$$x = \frac{ABS - 0.0177}{0.0749}$$

A.3 Calibration of lead from calibration curve

In order to determine the calibration curve of Pb^{2+} ion from lead nitrate solutions, the various concentrations of standard lead were prepared. The absorbance of Pb^{2+} ion from lead nitrate solutions was measured using atomic absorption spectrophotometer (AAS).

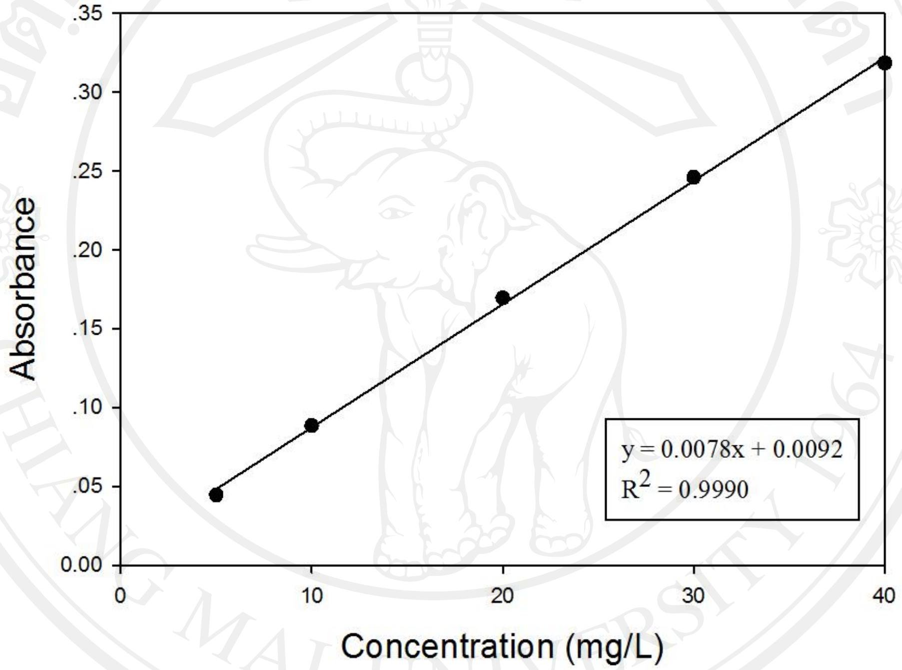

Figure A3 Calibration curve of lead

Equation of calibration curve: y = 0.0078x + 0.0092

When y = absorbance (ABS) and x = lead concentration

$$x = \frac{ABS - 0.0092}{0.0078}$$

A.4 Calibration of methylene blue from calibration curve

In order to determine the calibration curve of methylene blue, the various concentrations of standard methylene blue were prepared. The absorbance of methylene blue solutions were measured using UV-Vis spectrophotometer at 644 nm.

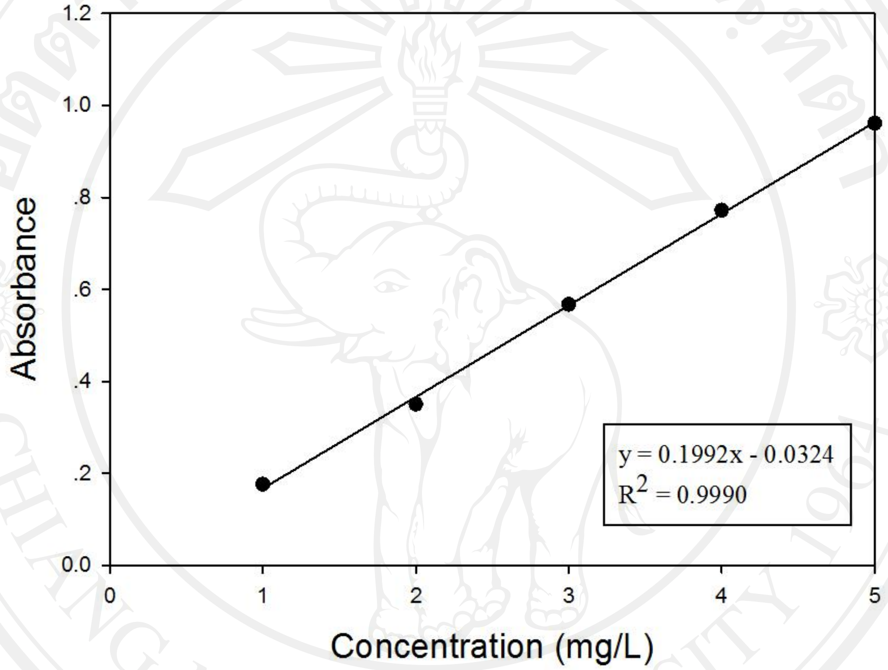

Figure A4 Calibration curve of methylene blue

Equation of calibration curve: y = 0.1992x - 0.0324

When y = absorbance (ABS) and x = lead concentration

$$x = \frac{ABS + 0.0324}{0.1992}$$

A.5 Calculation of the amount of adsorbed metal ion and the percentage of metal ions removal

The amount of adsorbed metal ion per gram of adsorbent was obtained using the following equation:

$$q_e = \frac{(C_i - C_e)}{M} V$$

The percentage of metal ion removal by adsorbent was calculated using the equation:

$$\%Removal = \frac{(C_i - C_e)}{C_i} \times 100$$

q_e = the amount of metal ion adsorbed per gram of adsorbent (mg/g)

C_i = the initial metal ion concentration of the solution (mg/L)

C_e = the equilibrium metal ion concentration or final metal concentration of the solution (mg/L)

V = volume of solution (L)

M = the mass of adsorbent used (g)

For example:

The copper concentration was calculated from equation of calibration curve.

The initial copper concentration at pH 6 was 50.00 mg/L

The equilibrium copper concentration at pH 6 was 20.16 mg/L

The volume of solution was 0.0500 L

The mass of adsorbent used was 0.400 g

$$q_e = \frac{(50.00 - 20.16)}{0.400} \times 0.0500$$

$$= 3.73\ mg/g$$

The amount of adsorbed copper ions was 3.73 mg/g

$$\%Removal = \frac{(C_i - C_e)}{C_i} \times 100$$

$$= \frac{(50.00 - 20.16)}{50.00} \times 100$$

$$= 59.7\%$$

The percentage of copper ions removal was 59.7%

APPENDIX B

Adsorption of Cu(II) ions on leonardite

B.1 Effect of pH

The adsorption of copper on leonardite was studied at a pH range of 2-6, the initial copper concentrations 5.00 and 20.00 mg/L, in order to investigate the optimum pH for the removal of this ion. All experiments were performed in five experiments.

Table B1 % Copper removal at pH 2-6 and the initial concentration of 5.00 mg/L

pH	**%Cu^{2+}Removal**				
	1	**2**	**3**	**4**	**5**
2	43.9	47.0	47.2	45.0	45.7
3	87.6	87.2	88.2	86.3	87.4
4	96.5	96.8	96.4	94.2	94.8
5	98.6	99.1	98.6	98.7	98.4
6	99.3	99.1	99.3	99.6	99.3

Table B2 % Copper removal at pH 2-6 and the initial concentration of 20.00 mg/L

pH	**%Cu^{2+}Removal**				
	1	**2**	**3**	**4**	**5**
2	12.8	8.4	18.2	11.9	8.5
3	58.1	56.6	60.2	51.2	51.2
4	69.8	72.3	78.4	76.2	78.1
5	81.4	79.5	81.8	81.0	84.2
6	91.9	89.2	90.9	91.7	92.7

B.2 Contact time

In order to study the effect of contact time on copper removal, the period of times were selected at 10, 20, 30, 40, 50, 60, 120, 180, 240, 300 and 360minutes, at 5.00 and 20.00 mg/L copper initial concentrations. All experiments were performed in five experiments.

Table B3 The amount of Cu^{2+} adsorbed vs. time at concentration of 5.00 mg/L

Time (min.)	The amount of Cu^{2+} adsorbed (mg/g)				
	1	2	3	4	5
0	0.0	0.0	0.0	0.0	0.0
10	0.5504	0.5624	0.5743	0.5653	0.5624
20	0.5533	0.5624	0.5743	0.5653	0.5638
30	0.5533	0.5650	0.5756	0.5680	0.5678
40	0.5558	0.5676	0.5769	0.5680	0.5678
50	0.5618	0.5676	0.5757	0.5668	0.5678
60	0.5606	0.5676	0.5791	0.5702	0.5689
120	0.5711	0.5738	0.5822	0.5775	0.5762
180	0.5730	0.5758	0.5832	0.5785	0.5782
240	0.5748	0.5794	0.5850	0.5803	0.5782
300	0.5765	0.5802	0.5850	0.5803	0.5798
360	0.5779	0.5809	0.5865	0.5818	0.5813

Table B4 The amount of Cu^{2+} adsorbed vs. time at concentration of 20.00 mg/L

Time (min.)	The amount of Cu^{2+} adsorbed (mg/g)				
	1	2	3	4	5
0	0	0	0	0	0
10	1.9299	1.9179	1.8896	1.9000	1.9179
20	1.9327	1.9151	1.8981	1.9029	1.9208
30	1.9381	1.9137	1.8994	1.9123	1.9261
40	1.9228	1.9163	1.8944	1.9034	1.9312
50	1.9241	1.9175	1.8967	1.9153	1.9240
60	1.9229	1.9197	1.9068	1.9176	1.9240
120	1.9824	1.9751	1.9611	1.9698	1.9658
180	1.9873	1.9780	1.9708	1.9746	1.9697
240	2.0061	1.9950	1.9833	1.9845	1.9777
300	2.0151	2.0024	1.9948	1.9869	1.9876
360	2.0188	2.0083	1.9985	2.0011	1.9913

B.3 Effect of leonardite quantity

In order to investigate the effect of leonardite quantity, a series of adsorption experiment was carried out with different leonardite dosages at the initial metal concentration of 5.00 and 20.00 mg/L. All experiments were performed in five experiments.

Table B5 %Copper removal at leonardite dose 0.400-3.00 g, at the initial concentration of 5.00 mg/L

Leonardite Quantity (g)	**%Cu^{2+} removal**				
	1	**2**	**3**	**4**	**5**
0.400	98.1	98.1	97.6	97.2	96.9
0.700	98.6	98.8	98.1	98.1	98.1
1.00	99.4	99.2	99.4	99.4	98.7
3.00	99.9	99.0	99.9	99.6	99.9

Table B6 % Copper removal at leonardite dose 0.400-3.00 g, at the initial concentration of 20.00 mg/L

Leonardite Quantity (g)	**%Cu^{2+} removal**				
	1	**2**	**3**	**4**	**5**
0.400	94.4	93.2	92.5	92.8	93.2
0.700	96.1	95.7	95.2	95.0	94.5
1.00	97.4	97.4	97.1	97.3	97.1
3.00	99.1	99.2	99.1	98.9	98.9

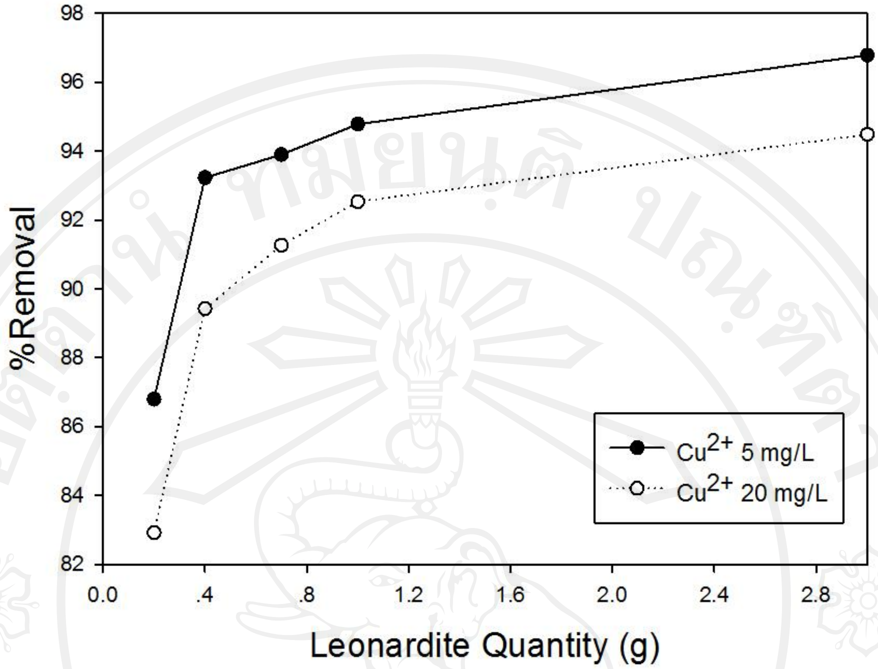

Figure B1 Effect of leonardite quantity at leonardite dose starting from 0.200-3.00 g at the two concentrations of Cu^{2+}

Table B7 %Copper removal at leonardite dose 0.200-3.00 g, at the two concentrations

Leonardite Quantity (g)	**%Cu^{2+} Removal**	
	Cu^{2+} 5 mg/L	**Cu^{2+} 20 mg/L**
0.200	86.8	82.9
0.400	93.2	89.4
0.700	93.9	91.3
1.00	94.8	92.5
3.00	96.8	94.5

B.4 Adsorption Isotherm

The adsorption capacity of adsorbent for copper was investigated over a range of copper concentrations. The experimental data for the uptake of Cu^{2+} ions by adsorbent over the studied concentration range were processed in accordance with the two of the most widely used adsorption isotherms: Langmuir and Freundlich isotherms.

First experiment

Table B8 Langmuir parameters for Cu^{2+}

Metal ions	Langmuir Isotherm					
	C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
Cu^{2+}	1.52	2.32	0.657	19.7	0.090	0.9864
	3.40	4.59	0.739			
	5.40	6.81	0.794			
	9.51	8.83	1.08			
	13.39	10.84	1.24			

Table B9 Freundlich parameters for Cu^{2+}

Metal ions	Freundlich Isotherm				
	$log\ C_e$	$log\ q_e$	K_F (mg L^{-1})	n	R^2
Cu^{2+}	0.183	0.365	1.85	1.4	0.9834
	0.531	0.662			
	0.733	0.833			
	0.978	0.946			
	1.13	1.04			

Second experiment

Table B10 Langmuir parameters for Cu^{2+}

Metal ions	Langmuir Isotherm					
	C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
Cu^{2+}	1.46	2.33	0.626	19.1	0.093	0.9704
	3.40	4.59	0.739			
	5.19	6.84	0.758			
	9.78	8.79	1.11			
	13.06	10.88	1.20			

Table B11 Freundlich parameters for Cu^{2+}

Metal ions	Freundlich Isotherm				
	log C_e	*log* q_e	K_F (mg L^{-1})	n	R^2
Cu^{2+}	0.164	0.367	1.92	1.4	0.9813
	0.531	0.662			
	0.715	0.835			
	0.990	0.944			
	1.12	1.04			

Third experiment

Table B12 Langmuir parameters for Cu^{2+}

Metal ions	Langmuir Isotherm					
	C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
Cu^{2+}	1.50	2.32	0.647	17.5	0.108	0.9611
	3.40	4.59	0.739			
	4.97	6.87	0.723			
	10.33	8.72	1.18			
	14.04	10.76	1.31			

Table B13 Freundlich parameters for Cu^{2+}

Metal ions	Freundlich Isotherm				
	log C_e	*log* q_e	K_F (mg L^{-1})	n	R^2
Cu^{2+}	0.366	0.176	1.96	1.5	0.9635
	0.662	0.531			
	0.837	0.696			
	0.941	1.01			
	1.03	1.15			

Fourth experiment

Table B14 Langmuir parameters for Cu^{2+}

Metal ions	Langmuir Isotherm					
	C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
Cu^{2+}	1.68	2.23	0.753	17.3	0.099	0.9343
	3.46	4.38	0.790			
	5.15	6.78	0.760			
	10.92	8.41	1.30			
	14.52	10.34	1.40			

Table B15 Freundlich parameters for Cu^{2+}

Metal ions	Freundlich Isotherm				
	$\log C_e$	$\log q_e$	K_F (mg L^{-1})	n	R^2
Cu^{2+}	0.226	0.349	1.79	1.5	0.9477
	0.539	0.641			
	0.712	0.831			
	1.04	0.925			
	1.16	1.01			

Fifth experiment

Table B16 Langmuir parameters for Cu^{2+}

Metal ions	Langmuir Isotherm					
	C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
Cu^{2+}	1.68	2.23	0.753	17.3	0.099	0.9343
	3.46	4.38	0.790			
	5.15	6.78	0.760			
	10.92	8.41	1.30			
	14.52	10.34	1.40			

Table B17 Freundlich parameters for Cu^{2+}

Metal ions	Freundlich Isotherm				
	log C_e	*log* q_e	K_F (mg L^{-1})	*n*	R^2
Cu^{2+}	0.226	0.349	1.79	1.5	0.9477
	0.539	0.641			
	0.712	0.831			
	1.04	0.925			
	1.16	1.01			

APPENDIX C

Adsorption of Zn(II) ions on leonardite

C.1 Effect of pH

The adsorption of zinc on leonardite was studied at a pH range of 2-6, the initial zinc concentrations of 5.00 and 20.00 mg/L, in order to investigate the optimum pH for the removal of this ion. All experiments were performed in five experiments.

TableC1 % Zinc removal at pH 2-6 and the initial concentration of 5.00 mg/L

pH	**%Zn^{2+}Removal**				
	1	**2**	**3**	**4**	**5**
2	5.7	9.1	6.9	5.2	6.8
3	11.9	14.2	12.6	11.1	13.0
4	22.7	21.6	20.5	19.7	20.6
5	29.3	29.9	29.9	28.5	29.6
6	43.6	43.4	41.7	45.1	43.7

TableC2 % Zinc removal at pH 2-6 and the initial concentration of 20.00 mg/L

pH	**%Removal**				
	1	**2**	**3**	**4**	**5**
2	2.9	6.2	2.1	2.1	3.6
3	11.3	11.8	10.3	11.0	13.0
4	22.2	19.9	18.8	17.3	20.6
5	28.9	25.2	24.9	26.0	29.6
6	38.2	42.3	40.4	36.9	43.7

C.2 Contact time

In order to study the effect of contact time on zinc removal, the period of times were selected at 10, 20, 30, 40, 50, 60, 120, 180, 240, 300 and 360minutes, at 5.00 and 20.00 mg/L zinc initial concentrations. All experiments were performed in five experiments.

Table C3 The amount of Zn^{2+} adsorbed vs. time at concentration of 5.00 mg/L

Time (min.)	The amount of Zn^{2+} adsorbed (mg/g)				
	1	2	3	4	5
0	0	0	0	0	0
10	0.2496	0.2491	0.2436	0.2538	0.2232
20	0.2589	0.2751	0.2674	0.2696	0.2597
30	0.2626	0.2931	0.2728	0.2717	0.2756
40	0.2662	0.2950	0.2815	0.2737	0.2815
50	0.2706	0.2988	0.2874	0.2806	0.2900
60	0.2748	0.3005	0.2902	0.2849	0.2928
120	0.3014	0.3076	0.2960	0.3008	0.2980
180	0.3306	0.3546	0.3315	0.3333	0.3402
240	0.3339	0.3574	0.3329	0.3375	0.3443
300	0.3339	0.3602	0.3337	0.3398	0.3497
360	0.3337	0.3613	0.3337	0.3405	0.3499

Table C4 The amount of Zn^{2+} adsorbed vs. time at concentration of 20.00 mg/L

Time (min.)	The amount of Zn^{2+} adsorbed (mg/g)				
	1	2	3	4	5
0	0	0	0	0	0
10	0.6862	0.6026	0.7030	0.5859	0.7615
20	0.7101	0.6741	0.7586	0.6415	0.7694
30	0.7477	0.7117	0.7962	0.6791	0.7995
40	0.8046	0.7331	0.8175	0.7005	0.8138
50	0.8246	0.7799	0.8443	0.7071	0.8204
60	0.8748	0.7924	0.8964	0.7322	0.8393
120	0.8982	0.8041	0.8752	0.7673	0.8451
180	0.9509	0.8623	0.9333	0.8255	0.8978
240	0.9526	0.8791	0.9401	0.8473	0.9196
300	0.9577	0.8841	0.9636	0.8570	0.9293
360	0.9709	0.8848	0.9725	0.8618	0.9383

C.3 Effect of leonardite quantity

In order to investigate the effect of leonardite quantity, a series of adsorption experiment was carried out with different leonardite dosages at the initial metal concentration of 5.00 and 20.00 mg/L. All experiments were performed in five experiments.

Table C5 %Zinc removal at leonardite dose 0.400-3.00 g, at the initial concentration of 5.00 mg/L

Leonardite Quantity (g)	**%Zn^{2+} removal**				
	1	**2**	**3**	**4**	**5**
0.400	40.0	43.2	41.6	40.6	41.8
0.700	49.4	47.8	47.2	45.9	49.9
1.00	66.8	68.0	67.9	64.3	66.9
3.00	85.2	84.1	87.0	83.6	87.8

Table C6 %Zinc removal at leonardite dose 0.400-3.00 g, at the initial concentration of 20.00 mg/L

Leonardite Quantity (g)	**%Zn^{2+} removal**				
	1	**2**	**3**	**4**	**5**
0.400	37.1	40.3	37.0	36.7	36.7
0.700	41.3	42.4	39.5	42.6	43.7
1.00	52.7	55.5	53.3	59.5	54.9
3.00	63.7	67.8	66.9	63.6	66.9

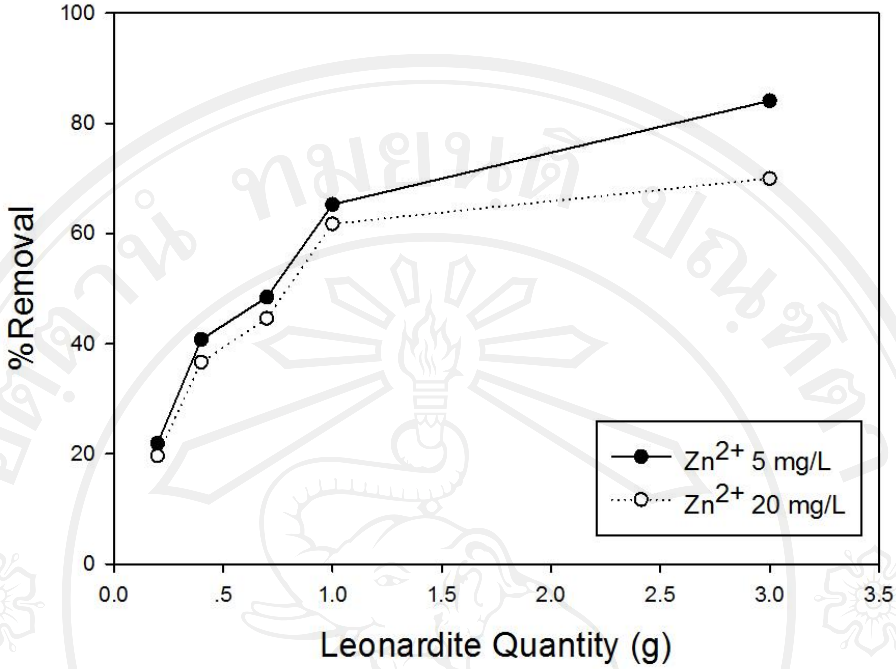

Figure C1 Effect of leonardite quantity at leonardite dose starting from 0.200-3.00 g at the two concentrations of Zn^{2+}

Table C7 %Zinc removal at leonardite dose 0.200-3.00 g, at the two concentrations

Leonardite Quantity (g)	**% Zn^{2+} Removal**	
	Zn^{2+} 5 mg/L	**Zn^{2+} 20 mg/L**
0.200	21.9	19.6
0.400	40.8	36.7
0.700	48.4	44.6
1.00	65.3	61.7
3.00	84.1	70.0

C.4 Adsorption Isotherm

The adsorption capacity of adsorbent for copper was investigated over a range of zinc concentrations. The experimental data for the uptake of Zn^{2+} ions by adsorbent over the studied concentration range were processed in accordance with the two of the most widely used adsorption isotherms: Langmuir and Freundlich isotherms.

First experiment

Table C8 Langmuir parameters for Zn^{2+}

Metal ions	Langmuir Isotherm					
	C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
Zn^{2+}	2.09	0.351	5.96	10.9	0.015	0.9360
	4.51	0.685	6.58			
	9.16	1.31	6.97			
	13.74	1.88	7.32			
	19.58	2.55	7.69			

Table C9 Freundlich parameters for Zn^{2+}

Metal ions	Freundlich Isotherm				
	$log\ C_e$	$log\ q_e$	K_F (mg L^{-1})	n	R^2
Zn^{2+}	1.14	0.274	0.330	1.5	0.9859
	1.29	0.406			
	1.50	0.535			
	1.64	0.653			
	1.77	0.694			

Second experiment

Table C10 Langmuir parameters for Zn^{2+}

Metal ions	Langmuir Isotherm					
	C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
Zn^{2+}	2.09	0.351	5.95	7.0	0.024	0.9119
	4.53	0.683	6.64			
	9.20	1.18	7.77			
	14.35	1.81	7.93			
	19.22	2.25	8.52			

Table C11 Freundlich parameters for Zn^{2+}

Metal ions	Freundlich Isotherm				
	$log\ C_e$	$log\ q_e$	K_F (mg L^{-1})	n	R^2
Zn^{2+}	1.16	0.258	0.254	1.3	0.9817
	1.28	0.353			
	1.50	0.517			
	1.63	0.654			
	1.77	0.688			

Third experiment

Table C12 Langmuir parameters for Zn^{2+}

Metal ions	Langmuir Isotherm					
	C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
Zn^{2+}	2.00	0.350	5.71	9.3	0.019	0.9227
	4.51	0.683	6.61			
	9.16	1.34	6.82			
	14.35	1.95	7.34			
	19.76	2.51	7.86			

Table C13 Freundlich parameters for Zn^{2+}

Metal ions	Freundlich Isotherm				
	$log\ C_e$	$log\ q_e$	K_F (mg L^{-1})	n	R^2
Zn^{2+}	1.16	0.291	0.315	1.4	0.9743
	1.30	0.400			
	1.51	0.542			
	1.63	0.673			
	1.77	0.697			

Fourth experiment

Table C14 Langmuir parameters for Zn^{2+}

Metal ions	Langmuir Isotherm					
	C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
Zn^{2+}	2.12	0.334	6.35	15.5	0.011	0.9120
	4.51	0.663	6.80			
	9.20	1.33	6.94			
	14.01	1.98	7.08			
	19.04	2.49	7.64			

Table C15 Freundlichparameters for Zn^{2+}

Metal ions	Freundlich Isotherm				
	$log\ C_e$	$log\ q_e$	K_F (mg L^{-1})	n	R^2
Zn^{2+}	1.15	0.296	0.326	1.5	0.9954
	1.28	0.396			
	1.50	0.548			
	1.63	0.634			
	1.75	0.705			

Fifth experiment

Table C16 Langmuir parameters for Zn^{2+}

Metal ions	Langmuir Isotherm					
	C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
Zn^{2+}	2.09	0.352	5.93	7.0	0.024	0.9492
	4.62	0.689	6.71			
	9.43	1.28	7.37			
	14.01	1.86	7.53			
	19.94	2.28	8.76			

Table C17 Freundlich parameters for Zn^{2+}

Metal ions	Freundlich Isotherm				
	$log\ C_e$	$log\ q_e$	K_F (mg L^{-1})	n	R^2
Zn^{2+}	1.15	0.270	0.284	1.4	0.9952
	1.30	0.357			
	1.52	0.519			
	1.64	0.628			
	1.77	0.692			

APPENDIX D

Adsorption of Pb(II) ions on leonardite

D.1 Effect of pH

The adsorption of lead on leonardite was studied at a pH range of 2-6, the initial lead concentrations 5.00 and 20.00 mg/L, in order to investigate the optimum pH for the removal of this ion. All experiments were performed in five experiments.

Table D1 % Lead removal at pH 2-6 and the initial concentration of 5.00 mg/L

pH	**%Pb^{2+}Removal**				
	1	**2**	**3**	**4**	**5**
2	84.7	83.8	85.1	81.8	81.6
3	99.8	99.8	99.8	99.8	99.8
4	99.8	99.8	99.8	99.8	99.8
5	99.8	99.8	99.8	99.8	99.8
6	99.8	99.8	99.8	99.8	99.8

Table D2 % Lead removal at pH 2-6 and the initial concentration of 20.00 mg/L

pH	**%Pb^{2+} Removal**				
	1	**2**	**3**	**4**	**5**
2	58.00	58.5	57.2	57.9	56.7
3	92.0	89.4	90.00	90.8	90.6
4	98.8	98.1	98.4	97.5	97.4
5	99.9	99.9	99.9	99.9	99.9
6	99.9	99.9	99.9	99.9	99.9

D.2 Contact time

In order to study the effect of contact time on lead removal, the period of times were selected at 10, 20, 30, 40, 50, 60, 120, 180, 240, 300 and 360minutes, at 5.00 and 20.00 mg/L lead initial concentrations. All experiments were performed in five experiments.

Table D3 The amount of Pb^{2+} adsorbed vs. time at concentration of 5.00 mg/L

Time (min.)	**The amount of Pb^{2+} adsorbed (mg/g)**				
	1	**2**	**3**	**4**	**5**
0	0	0	0	0	0
10	0.5209	0.5129	0.4969	0.5049	0.4969
20	0.5285	0.5357	0.5273	0.5277	0.5197
30	0.5381	0.5381	0.5369	0.5373	0.5365
40	0.5381	0.5381	0.5369	0.5373	0.5365
50	0.5381	0.5381	0.5369	0.5373	0.5365
60	0.5381	0.5381	0.5369	0.5373	0.5365
120	0.5381	0.5381	0.5369	0.5373	0.5365
180	0.5381	0.5381	0.5369	0.5373	0.5365
240	0.5381	0.5381	0.5369	0.5373	0.5365
300	0.5381	0.5381	0.5369	0.5373	0.5365
360	0.5381	0.5381	0.5369	0.5373	0.5365

Table D4 The amount of Pb^{2+} adsorbed vs. time at concentration of 20.00 mg/L

Time (min.)	**The amount of Pb^{2+} adsorbed (mg/g)**				
	1	**2**	**3**	**4**	**5**
0	0	0	0	0	0
10	2.3798	2.3448	2.3478	2.3397	2.3718
20	2.3874	2.4091	2.4010	2.3702	2.3946
30	2.4235	2.4091	2.4227	2.3918	2.3946
40	2.4303	2.4295	2.4227	2.4054	2.4219
50	2.4452	2.4295	2.4440	2.4396	2.4283
60	2.4452	2.4434	2.4440	2.4516	2.4422
120	2.4452	2.4434	2.4440	2.4534	2.4422
180	2.4452	2.4434	2.4440	2.4534	2.4422
240	2.4452	2.4434	2.4440	2.4534	2.4422
300	2.4452	2.4434	2.4440	2.4534	2.4422
360	2.4452	2.4434	2.4440	2.4534	2.4422

D.3 Effect of leonardite quantity

In order to investigate the effect of leonardite quantity, a series of adsorption experiment was carried out with different leonardite dosages at the initial metal concentration of 5.00 and 20.00 mg/L. All experiments were performed in five experiments.

Table D5 %Lead removal at leonardite dose 0.400-3.00 g, at the initial concentration of 5.00 mg/L

Leonardite Quantity (g)	**%Pb^{2+} removal**				
	1	**2**	**3**	**4**	**5**
0.400	99.8	99.8	99.8	99.8	99.8
0.700	99.8	99.8	99.8	99.8	99.8
1.00	99.8	99.8	99.8	99.8	99.8
3.00	99.8	99.8	99.8	99.8	99.8

Table D6 %Lead removal at leonardite dose 0.400-3.00 g, at the initial concentration of 20.00 mg/L

Leonardite Quantity (g)	**%Pb^{2+} removal**				
	1	**2**	**3**	**4**	**5**
0.400	99.1	99.2	99.2	99.2	99.2
0.700	99.9	99.9	99.9	99.9	99.9
1.00	99.9	99.9	99.9	99.9	99.9
3.00	99.9	99.9	99.9	99.9	99.9

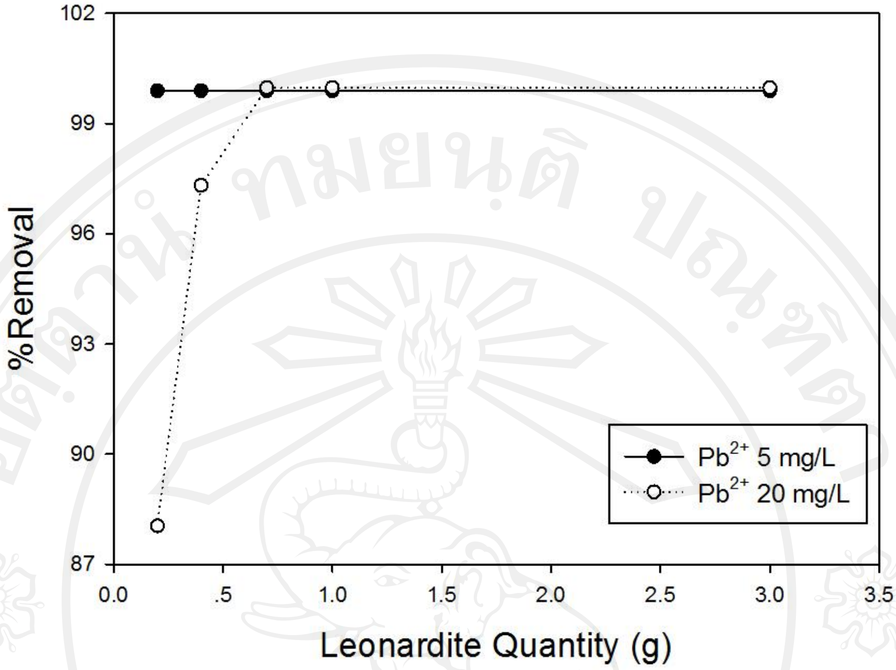

Figure D1 Effect of leonardite quantity at leonardite dose starting from 0.200-3.00 g at the two concentrations of Pb^{2+}

Table D7 %Lead removal at leonardite dose 0.200-3.00 g, at the two concentrations

Leonardite Quantity (g)	%Pb^{2+}Removal	
	Pb^{2+} 5 mg/L	Pb^{2+}20 mg/L
0.200	99.8	88.1
0.400	99.8	97.3
0.700	99.8	99.9
1.00	99.8	99.9
3.00	99.8	99.9

D.4 Adsorption Isotherm

The adsorption capacity of adsorbent for lead was investigated over a range of lead concentrations. The experimental data for the uptake of Pb^{2+} ions by adsorbent over the studied concentration range were processed in accordance with the two of the most widely used adsorption isotherms: Langmuir and Freundlich isotherms

First experiment

Table D8 Langmuir parameters for Pb^{2+}

Metal ions	Langmuir Isotherm					
	C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
Pb^{2+}	0.652	2.39	0.272	16.1	0.260	0.9942
	1.61	4.63	0.347			
	2.67	6.36	0.420			
	4.36	8.85	0.492			
	7.73	10.65	0.726			

Table D9 Freundlich parameters for Pb^{2+}

Metal ions	Freundlich Isotherm				
	log C_e	*log* q_e	K_F (mg L^{-1})	*n*	R^2
Pb^{2+}	- 0.186	0.379	3.32	1.6	0.9843
	0.206	0.665			
	0.427	0.803			
	0.639	0.947			
	0.888	1.03			

Second experiment

Table D10 Langmuir parameters for Pb^{2+}

Metal ions	Langmuir Isotherm					
	C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
Pb^{2+}	0.652	2.40	0.271	16.9	0.239	0.9958
	1.66	4.65	0.358			
	2.62	6.37	0.411			
	4.81	8.94	0.538			
	7.67	11.00	0.698			

Table D11 Freundlich parameters for Pb^{2+}

Metal ions	Freundlich Isotherm				
	$log\ C_e$	$log\ q_e$	K_F (mg L^{-1})	n	R^2
Pb^{2+}	- 0.186	0.381	3.29	1.6	0.9922
	0.221	0.667			
	0.418	0.804			
	0.682	0.951			
	0.885	1.04			

Third experiment

Table D12 Langmuir parameters for Pb^{2+}

Metal ions	Langmuir Isotherm					
	C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
Pb^{2+}	0.708	2.35	0.302	16.9	0.241	0.9939
	1.44	4.63	0.311			
	2.67	6.54	0.409			
	4.81	8.99	0.535			
	7.45	10.86	0.686			

Table D13 Freundlich parameters for Pb^{2+}

Metal ions	Freundlich Isotherm				
	$log\ C_e$	$log\ q_e$	K_F (mg L^{-1})	n	R^2
Pb^{2+}	- 0.150	0.370	3.27	1.6	0.9749
	0.158	0.665			
	0.427	0.816			
	0.682	0.954			
	0.872	1.04			

Fourth experiment

Table D14 Langmuir parameters for Pb^{2+}

Metal ions	Langmuir Isotherm					
	C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
Pb^{2+}	0.652	2.33	0.280	16.5	0.257	0.9961
	1.44	4.65	0.309			
	2.62	6.59	0.397			
	4.92	9.01	0.546			
	7.39	10.95	0.675			

Table D15 Freundlich parameters for Pb^{2+}

Metal ions	Freundlich Isotherm				
	log C_e	*log* q_e	K_F (mg L^{-1})	*n*	R^2
Pb^{2+}	- 0.186	0.368	3.36	1.6	0.9804
	0.158	0.667			
	0.418	0.819			
	0.692	0.955			
	0.867	1.04			

Fifth experiment

Table D16 Langmuir parameters for Pb^{2+}

Metal ions	Langmuir Isotherm					
	C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
	0.596	2.37	0.252			
	1.44	4.58	0.314			
Pb^{2+}	2.67	6.70	0.399	15.9	0.281	0.9978
	4.81	8.99	0.535			
	7.67	11.00	0.698			

Table D17 Freundlich parameters for Pb^{2+}

Metal ions	Freundlich Isotherm				
	log C_e	*log* q_e	K_F (mg L^{-1})	n	R^2
	- 0.225	0.374			
	0.158	0.661			
Pb^{2+}	0.427	0.826	3.46	1.7	0.9878
	0.682	0.954			
	0.885	1.04			

APPENDIX E

Adsorption of methylene blue on leonardite

E.1 Contact time

In order to study the effect of contact time on methylene blue removal, the period of times were selected at 10, 20, 30, 40, 50, 60, 120, 180, 240 and 300 minutes, at 60.00 and 110.0 mg/L methylene blue initial concentrations. All experiments were performed in five experiments.

Table E1 The amount of methylene blue adsorbed vs. time at concentration of 60.00 mg/L, using unwashed leonardite

Time (min.)	**The amount of methylene blue adsorbed (mg/g)**				
	1	**2**	**3**	**4**	**5**
0	0	0	0	0	0
10	7.1599	6.9036	6.6343	6.7876	6.8959
20	7.1688	6.9951	6.6505	6.8005	6.9984
30	7.1886	7.0384	6.7579	6.8462	7.0297
40	7.2179	7.0548	6.7637	6.8664	7.0540
50	7.2280	7.1036	6.7800	6.8853	7.0819
60	7.3497	7.2457	7.0560	7.1731	7.2636
120	7.4028	7.3616	7.2732	7.3006	7.3582
180	7.4036	7.3629	7.2772	7.3072	7.3606
240	7.4036	7.3633	7.2780	7.3096	7.3610
300	7.4040	7.3633	7.2784	7.3122	7.3614

Table E2 The amount of methylene blue adsorbed vs. time at concentration of 60.00 mg/L, using washed leonardite

Time (min.)	The amount of methylene blue adsorbed (mg/g)				
	1	**2**	**3**	**4**	**5**
0	0	0	0	0	0
10	6.6378	6.3726	6.0147	6.2080	6.3521
20	6.6378	6.4946	6.1573	6.3753	6.4124
30	6.6604	6.5062	6.1941	6.4606	6.5151
40	6.6924	6.6480	6.2405	6.5297	6.5582
50	6.7727	6.7508	6.3496	6.5838	6.6292
60	6.9817	7.0435	6.8861	6.8753	6.9836
120	7.2473	7.2405	7.1401	7.1946	7.2178
180	7.2481	7.2409	7.1454	7.1990	7.2182
240	7.2488	7.2413	7.1462	7.2011	7.2186
300	7.2488	7.2413	7.1462	7.2025	7.2200

Table E3 The amount of methylene blue adsorbed vs. time at concentration of 110.0 mg/L, using unwashed leonardite

Time (min.)	The amount of methylene blue adsorbed (mg/g)				
	1	**2**	**3**	**4**	**5**
0	0	0	0	0	0
10	9.2372	9.0832	8.8233	8.8857	8.7145
20	9.2610	9.1551	8.8978	8.9812	8.8830
30	9.2837	9.4050	9.1569	9.1168	9.0883
40	9.6679	9.6624	9.3570	9.3090	9.1314
50	9.8487	9.6422	9.4198	9.4095	9.3139
60	9.7734	9.9072	9.6160	9.5791	9.4279
120	11.8980	11.9022	11.7912	11.7759	11.7116
180	12.4256	12.4192	12.3308	12.3366	12.2803
240	12.4316	12.4249	12.3406	12.3381	12.2867
300	12.4340	12.4277	12.3449	12.3395	12.2958

Table E4 The amount of methylene blue adsorbed vs. time at concentration of 110.0 mg/L, using washed leonardite

Time (min.)	**The amount of methylene blue adsorbed (mg/g)**				
	1	**2**	**3**	**4**	**5**
0	0	0	0	0	0
10	9.5637	9.4365	9.1111	9.4133	9.1960
20	9.7545	9.5804	9.6082	9.5327	9.3886
30	9.8449	9.7848	9.7259	9.6683	9.5255
40	9.9517	9.8277	9.9928	9.7538	9.6332
50	9.9517	9.9287	10.1812	9.8342	9.8156
60	9.8952	10.0044	10.3186	9.8719	9.3487
120	12.2395	12.2180	12.5738	12.1785	12.5148
180	12.5300	12.5168	12.8830	12.4808	12.4628
240	12.5368	12.5232	12.8842	12.4872	12.4677
300	12.5378	12.5246	12.8863	12.4921	12.4705

E.2 Effect of leonardite quantity

In order to investigate the effect of leonardite quantity, a series of adsorption experiment was carried out with different leonardite dosages at the initial methylene blue concentration of 60.00 and 110.0 mg/L. All experiments were performed in five experiments.

Table E5 %Methylene blue removal at leonardite dose 0.200-3.00 g, at the initial concentration of 60.00 mg/L

Leonardite Quantity (g)	**%Methylene blue removal**				
	1	**2**	**3**	**4**	**5**
0.200	99.5	99.5	99.5	99.4	99.4
0.400	99.7	99.7	99.6	99.6	99.6
0.700	99.7	99.7	99.7	99.6	99.6
1.00	99.7	99.7	99.7	99.7	99.7
3.00	99.7	99.7	99.7	99.7	99.7

Table E6 %Methylene blue removal at leonardite dose 0.2-3 g, at the initial concentration 110 mg/L

Leonardite Quantity (g)	**%Methylene blue removal**				
	1	**2**	**3**	**4**	**5**
0.200	92.8	99.2	99.0	95.1	93.8
0.400	99.7	99.6	99.6	99.7	99.6
0.700	99.7	99.7	99.7	99.8	99.7
1.00	99.8	99.8	99.7	99.8	99.6
3.00	99.8	99.8	99.8	99.8	99.8

Table E7 The amount of methylene blue adsorbed at leonardite dose 0.200-3.00 g, at the initial concentration 60.00 mg/L

Leonardite Quantity (g)	The amount of methylene blue adsorbed				
	1	**2**	**3**	**4**	**5**
0.200	14.9209	14.9297	14.9246	14.907	14.9096
0.400	7.4755	7.4736	7.4705	7.4709	7.4697
0.700	4.2728	4.2717	4.2707	4.2698	4.2695
1.00	2.9917	2.9902	2.9902	2.9897	2.9897
3.00	0.9972	0.9970	0.9968	0.9966	0.9966

Table E8 The amount of methylene blue adsorbed at leonardite dose 0.200-3.00 g, at the initial concentration of 110 mg/L

Leonardite Quantity (g)	The amount of methylene blue adsorbed				
	1	**2**	**3**	**4**	**5**
0.200	25.5174	25.3639	25.3110	26.1465	25.7967
0.400	13.7041	13.6972	13.6947	13.7123	13.6960
0.700	7.8349	7.8299	7.8309	7.8385	7.8324
1.00	5.4884	5.4879	5.4839	5.4879	5.4864
3.00	1.8301	1.8295	1.8297	1.8298	1.8298

E.3 Adsorption Isotherm

First experiment

Table E9 Langmuir parameters for methylene blue isotherm

Methylene blue	**Langmuir Isotherm**					
	C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
	0.247	9.97	0.024			
	0.263	12.47	0.021			
	0.482	14.94	0.032			
	0.517	17.44	0.030	26.4	3.3	0.9976
	0.578	19.93	0.029			
	1.79	22.28	0.080			
	4.01	24.50	0.164			

Table E10 Freundlich parametersfor methylene blue isotherm

Methylene blue	Freundlich Isotherm				
	log C_e	*log* q_e	K_F (mg L^{-1})	*n*	R^2
	-0.625	0.999			
	-0.580	1.10			
	-0.317	1.17	18.6	3.6	0.7982
	-0.286	1.24			
	-0.238	1.30			
	0.253	1.35			
	0.603	1.39			

Second experiment

Table E11 Langmuir parameters for methylene blue isotherm

Methylene blue	**Langmuir Isotherm**					
	C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
	0.242	9.97	0.024			
	0.263	12.47	0.021			
	0.451	14.94	0.030	26.6	3.2	0.9979
	0.568	17.43	0.033			
	0.624	19.92	0.031			
	1.72	22.28	0.077			
	3.80	24.52	0.155			

Table E12 Freundlich parameters for methylene blue isotherm

Methylene blue	Freundlich Isotherm				
	log C_e	*log* q_e	K_F (mg L^{-1})	*n*	R^2
	-0.616	0.999			
	-0.580	1.10			
	-0.346	1.17	18.6	3.4	0.8244
	-0.245	1.24			
	-0.205	1.30			
	0.237	1.35			
	0.580	1.39			

Third experiment

Table E13 Langmuir parameters for methylene blue isotherm

Methylene blue	**Langmuir Isotherm**					
	C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
	0.258	9.97	0.027			
	0.309	12.46	0.025			
	0.482	14.94	0.032	26.6	3.0	0.9981
	0.584	17.43	0.033			
	0.680	19.91	0.034			
	1.75	22.28	0.079			
	4.22	24.47	0.173			

Table E14 Freundlich parameters for for Methylene blue isotherm

Methylene blue	Freundlich Isotherm				
	log C_e	*log* q_e	K_F (mg L^{-1})	*n*	R^2
	-0.589	0.999			
	-0.511	1.10			
	-0.317	1.17	18.2	3.4	0.8166
	-0.234	1.24			
	-0.167	1.30			
	0.244	1.35			
	0.626	1.39			

Fourth experiment

Table E15 Langmuir parameters for methylene blue isotherm

Methylene blue	**Langmuir Isotherm**					
	C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
	0.229	9.97	0.023			
	0.249	12.47	0.020			
	0.451	14.94	0.030	26.2	3.4	0.9984
	0.561	17.43	0.032			
	0.607	19.92	0.030			
	1.75	22.28	0.078			
	4.13	24.48	0.169			

Table E16 Freundlich parameters for for Methylene blue isotherm

Methylene blue	**Freundlich Isotherm**				
	log C_e	*log* q_e	K_F (mg L^{-1})	*n*	R^2
	-0.639	0.999			
	-0.603	1.10			
	-0.346	1.17	18.6	3.6	0.8192
	-0.251	1.24			
	-0.217	1.30			
	0.243	1.35			
	0.616	1.39			

Fifth experiment

Table E17 Langmuir parameters for methylene blue isotherm

Methylene blue	**Langmuir Isotherm**					
	C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
	0.204	9.97	0.020			
	0.234	12.47	0.019			
	0.451	14.94	0.030	26.1	3.6	0.9986
	0.521	17.43	0.030			
	0.597	19.93	0.030			
	1.80	22.28	0.081			
	4.08	24.49	0.167			

Table E18 Freundlich parameters for for Methylene blue isotherm

Methylene blue	Freundlich Isotherm				
	log C_e	*log* q_e	K_F (mg L^{-1})	*n*	R^2
	-0.690	0.999	18.7	3.7	0.8325
	-0.630	1.10			
	-0.346	1.17			
	-0.283	1.24			
	-0.224	1.30			
	0.255	1.35			
	0.611	1.39			

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