Evaluation of Egyptian adsorbent agents technology for the removal of PCBs in aqueous solution

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Abstracts

Four Egyptian clay minerals (bentonite, montmorillonite, zeolite and kaolinite) were tested for its physicochemical properties and studying their ability to adsorb PCBs in aqueous solution. The results indicated that bentonite had a higher percentage of CaO and Na_2O however the highest percentage of Al_2O_3 was found in Kaolinite. Ferric oxide was found in a high percentage in montmorillonite. Moreover, the results indicated that bentonite had the highest specific surface area compared with the other tested clays. Meanwhile montmorillonite, kaolinite and zeolite had a high methylene blue value compared with bentonite. In addition, zeolite had the highest Cation Exchange Capacity (CEC) whereas, kaolonite and bentonite had the same CEC. Due to its higher surface area, bentonite was selected to be tested for the ability to adsorb and remove of PCBs in aqueous solutions. The results revealed that addition of benonite at 0.5 and 1.0 % (w/v) resulted in the removal of 64.17 and 55.13 % of PCB congeners in aqueous solution, respectively as determined by GC. The adsorption capacity of bentonite to PCBs showed a variation depending on the number of chlorine atoms substituted on the biphenyl rings. It was higher with the high chlorinated PCBs than the low chlorinated PCBs.

Introduction

Polychlorinated biphenyls (PCBs) are environmental contaminants that had been widely used for various industrial purposes. More than 1.2 million metric tons of PCBs were produced world-wide between 1929 and 1977[1], however the production had been banned in most countries thereafter. In Egypt, PCBs were never produced, although the use of these substances certain industries was common[2]. Being lipophilic, PCBs accumulate and persist in fluids and tissues. Exposure to these compounds results in various harmful effects including reproductive toxicity, immune suppression, birth defects, cancer, developmental and behavioral changes[3]. The number and location of chlorine atoms introduced into the biphenyl molecule determine the potency and nature of the toxicity of each PCB[4]. Because the PCBs may significantly affect animal and human health, removal of these toxic substances is a critical need. The use of clay minerals to remove chemical contaminants had been increasingly paid attention due to its effectively cost than other materials. Clays are widely applied in many fields of technology and science[5] and its play an important role in the removal of heavy metals, natural organic matter and synthetic organic compounds[6] These sorbents are widely used due to their high specific surface areas associated with their small particle size, low cost, and ubiquitous occurrence in most soil and sediment environments[7,8].

MATERIALS & METHODS

Chemicals

DCMA Polychlorinated biphenyl mixtures IUPAC nos. 1, 11 (100 µg/ml for each), 29, 47, 116, 135 (10 µg/ml for each), 185, 194, 206 and 209 (5 µg/ml for each) were purchased from Supelco Company (Supelco Park, Bellefonte, PA. U.S.A). Hexane and dichloromethane were of Supra Solv grade, anhydrous sodium sulphate was obtained from Merck (Darmstadt, Germany).

Sorbent materials

Bentonite, montmorillonite, zeolite and kaolinite were provided by the Ceramic Department, National Research Center, Cairo, Egypt.

Determination of physicochemical parameters of clay

The oxide composition was determined by the X-ray fluorescence technique (XRF) for element analysis. The specific surface area in m^2/g was determined by using a modified volumetric apparatus of the BET (Brunauer, Emmett and Teller) type[9]. Methylene Blue Adsorption value and Cation Exchange Capacity (CEC) were determined by the spot method according to Taylor[10].

Determination of adsorption abilities

The determination of the adsorption capability of sorbent materials with high specific surface area was carried out according to the method described by Aly *et al.*[11]. The remaining residues of PCB congeners in the aqueous solution were determined by GC according to Blanchard *et al.*[12].

Statistical analyses

All data were subjected to statistical analyses using the General Linear Models (GLM) Procedure of the Statistical Analysis System[13]. The significance of the differences among treatment groups with variable means was determined by the Waller-Duncan k-ratio T test[14]. All statements of significance were based on a probability level of $P \leq 0.05$.

Results & Discussions

Clays analyses

The data in Table (1) revealed the oxide composition of the tested Egyptian clays clearly indicated that bentonite had a higher percentage of CaO and Na_2O. The highest percentage of AL_2O_3 was found in kaolinite whereas, the lowest percentage was found in bentonite. Ferric oxide was found in a high percentage in montmorillonite followed by bentonite clay whereas, the lowest percentage was found in zeolite. Generally, Kaolinite contained the highest percentage in total oxide composition (85.22 %) followed by montmorillonite (82.53 %) and bentonite (81.38 %) whereas, zeolite clay contained the lowest percentage of the total oxide composition (75.22 %).

Table (1): Oxide composition of different tested clays

Oxide %	Zeolite	Mon.	Kaolinite	Bentonite
CaO	0.42	0.99	0.29	1.36
SiO_2	53.35	43.90	51.76	49.82
Al_2O_3	18.67	18.64	31.49	15.94
Fe_2O_3	0.35	9.50	1.37	8.67
MgO	-	2.04	-	1.64
SO_3	0.04	0.07	0.045	0.17
K_2O	-	1.08	0.10	0.93
Na_2O	2.21	2.10	0.07	2.56
Cl^-	0.18	4.21	0.09	0.29
Total	**75.22**	**82.53**	**85.22**	**81.38**

Mon. = Montmorillonite

The results of Specific Surface Area (SSA), Cation Exchange Capacity (CEC) and Methylene Blue Index (MBI) were showed in Figures 1-3 indicated that bentonite had the highest Specific Surface Area (SSA) (84.75 m^2/g) compared with the other tested clays. Meanwhile, no significant differences were found between the other tested clays (Fig. 1). Also the current results indicated that zeolite had the highest cation exchange capacity (CEC) followed by montmorillonite whereas kaolinite and bentonite had the same CEC (Fig. 2). The higher adsorption for methylene blue was found in montmorillonite, kaolinite and zeolite, while it was low for bentonite (48 mg/100g) (Fig. 3).
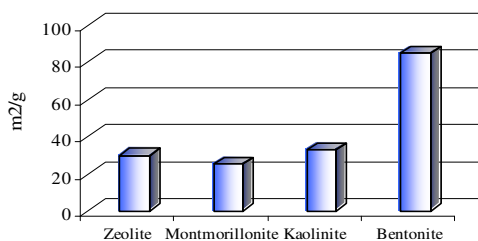

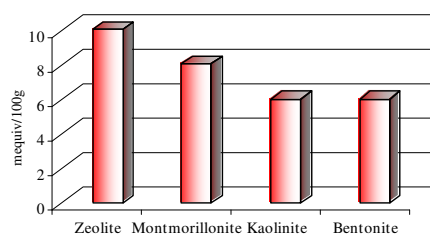Fig. 1. Specific Surfce Area (SSA)
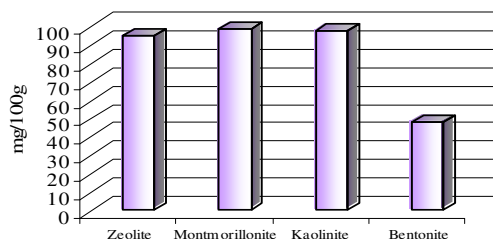

Fig.2 Cation Exchange Capacity

Fig. 3. Methylene Blue Value

Previous reports indicated that the adsorption capacity of the adsorbent is dependent mainly on the surface area. In the same concern the factors influencing adsorption of pesticides in soil were clarified that the clay with the larger surface area had the higher adsorption capacity[15]. Moreover, clay with a large surface area could adsorb organic compounds in each of the layers[16]. Galvano et al.[17] reported that regressions showed significant correlations of chemical adsorption with the physiochemical properties of the clays. Abdel-Wahhab et al.[18] reported that the significant amount of MB may indicate the presence of swelling clay which consequently increases the surface area resulting in a significant increase in the adsorption capacity of the clay for different chemicals[19]. Different studies have indicated that methylene blue Value (MBV) is a reliable and simple method to obtain information on the presence and properties of clay minerals, especially in the first stage of research. Furthermore, the adsorption of methylene blue from the aqueous phase is a useful tool for product control of sorbent and adsorption capacity depends not only on the porous structure of the adsorbent but also on its chemical structure[19].

In the current study, bentonite was found to have a larger surface area (Fig.1). From this point of view, bentonite was selected to be tested for its ability to adsorb and remove of PCBs from aqueous solution.

Adsorption of PCB congeners to bentonite *in vitro*

The ability of bentonite to bind total PCBs was studied *in vitro*. Our results clearly indicated that bentonite was capable of sorbing PCB congeners from aqueous solutions. Results given in Table (2) showed that bentonite had a high affinity for total PCBs and the adsorption ability was not significantly affected by the bentonite concentrations. The results illustrated that addition of bentonite at 0.5 % w/v (5 g bentonite /L) resulted in the removal of 64.17 % of total amount of PCB congeners in aqueous solution that was spiked with 40.58 ppb (40.58 µg/L), as determined by GC before treatment, whereas, addition of bentonite at 1.0 % (w/v) resulted in the removal of 55.13 % of the total amount of PCB congeners at the same concentration.

The results presented in Table (2) indicated that, addition of 0.5 and 1.0 % of bentonite resulted a variation in the binding of PCB congeners depending on the number of chlorine atoms substituted on the biphenyl rings. The percentage of reduction of individual PCB congeners (PCB nos. 1, 11, 29, 47, 116, 135, 185, 194, 206 and 209) ranged from 58.16 % to 90.31 % when 0.5 % of bentonite was added and ranged from 45.91 % to 84.69 % with 1.0 % of bentonite. Moreover, the results indicated that bentonite showed a higher binding capacity to PCB conger no. 209 (decachloro biphenyls) in the two tested levels (90.31 and 84.69 % with addition of 0.5 and 1.0 % of bentinite, respectively). However, bentonite showed a less binding capacity to PCB congener nos. 1, 11, 29 and 47.

Table (2): Adsorption of PCBs to bentonite at different levels in aqueous solutions (Mean ± SE).

PCB congener No.	PCB residues (µg/L) (Control)	PCB residues			
		0.5 % bentonite		1.0 % bentonite	
		Concentration (µg/L)	% Reduction	Concentration (µg/L)	% Reduction
1	$20.76^a \pm 3.03$	$7.53^b \pm 0.75$	63.73 %	$9.44^b \pm 2.12$	54.53 %
11	$13.19^a \pm 0.39$	$5.22^b \pm 0.22$	60.42 %	$7.13^b \pm 0.27$	45.94 %
29	$0.45^a \pm 0.02$	$0.12^b \pm 0.02$	72.67 %	$0.18^b \pm 0.03$	60.89 %
47	$1.96^a \pm 0.01$	$0.82^b \pm 0.06$	58.16 %	$0.36^b \pm 0.08$	81.63 %
116	$0.82^a \pm 0.05$	$0.22^b \pm 0.02$	73.49 %	$0.26^b \pm 0.005$	68.79 %
135	$1.21^a \pm 0.06$	$0.13^b \pm 0.04$	89.25 %	$0.23^b \pm 0.04$	80.66 %
185	$0.49^a \pm 0.04$	$0.08^b \pm 0.005$	83.27 %	$0.15^b \pm 0.01$	69.39 %
194	$0.43^a \pm 0.05$	$0.07^b \pm 0.01$	83.02 %	$0.12^b \pm 0.01$	72.09 %
206	$0.95^a \pm 0.01$	$0.32^b \pm 0.07$	66.31 %	$0.29^b \pm 0.01$	69.47 %
209	$0.32^a \pm 0.03$	$0.03^b \pm 0.009$	90.31 %	$0.049^b \pm 0.004$	84.69 %
Total PCBs	$\mathbf{40.58^a \pm 2.88}$	$\mathbf{14.54^b \pm 0.73}$	**64.17 %**	$\mathbf{18.21^{\,b} \pm 2.04}$	**55.13 %**

Within each row, means superscript with different letters are significantly different ($p < 0.05$).
Previous report[20] indicated that, the polarity of PCBs, and their affinity towards the aqueous phase, decreased with increasing chlorine substitution. These authors stated that the amount

of PCBs adsorbed from water for a given equilibrium concentration should increase in the order of tetrachlorobiphyls (TCB) to Heptachlorobiphenyls (HeCB). In accordance with these results, the current results indicated that the adsorption capacity for the high chlorinated PCBs was higher than the adsorption capacity for the low chlorinated PCBs. Accordingly, the higher adsorption capacity of bentonite for PCBs reported in the current study may be due to the large surface area of bentonite, which increased the adsorption of organic compounds in each of its layers[11]. Moreover[21] reported that montomorillonite had the property of adsorbing organic substances either on its external surfaces or within its interlaminar spaces by interaction with or substitution for the exchange cations present in their spaces. In the same concern, Carroll[22] reported that phyllosilicates are composed of layers of lattice silicates and chain silicates. These silicates were essentially comprised of repeating layers of (1) divalent or trivalent cations (e.g. aluminas) held in octahedral coordination with oxygens and hydroxyls, and (2) silicas that are tetrahedrally coordinated with oxygens and hydroxyls. In general, we can concluded that bentonite may possess three types of active binding sites: (1) those located at basal planes within interlayer channels, (2) those located on the surface, and (3) those located at the edges of clay particles which explained the higher affinity of bentonite to PCBs.

REFERENCES

1. WHO. Environmental Health Criteria 140. World Health Organization, Geneva; 1993 682 pp.
2. Barakat, AO, Kim, M, Qian, Y, Wade, TL. Baseline/Marine Pollution Bulletin. 2002; 44: 1421 –1434.
3. Safe, SH. Crit. Rev. Toxicol. 1994; 24: 87-149.
4. Robertson, LW, Hansen, LG. University Press of Kentucky, Lexington, KY.; 2001.
5. Lin, S, Juang, RS. J. Hazardous Mat. 2002; B92: 315-326.
6. Jiang, J, Zeng, Z. Chemosphere 2003; 53: 53-62.
7. Celis, R, Hermosin, MC, Carrizosa, MJ, Cornejo, J. J. Agric. Food Chem. 2002; 50: 2324-2330.
8. Lagaly, G. Appl. Clay Sci. 2001; 18: 223-231.
9. Brunauer, S, Emmett, PH, Teller, E. J. Amer. Chem. Soc. 1938; 60: 309.
10. Taylor, RK. J. Chem. Tech. Biotechnol. 1985; 35A: 195-207.
11. Aly, SE., Abdel-Galil, MM, Abdel-Wahhab, MA. Food and Chem. Toxicol. 2004; 42: 1825- 1831.
12. Blanchard, M, Teil, MJ, Carru, AM, Garban, B, Ollivon, D, Chesterikoff, A, Chevreuil, M. Hydrobiologia 1999; 400: 149-154.
13. SAS Institute. *SAS User's Guide*: Statistics. 1982 Edition, SAS Institute Inc., Cary, NC.
14. Waller, RA, Duncan, DB. I. Am. State Assoc. 1969; 64: 1484-1503.
15. Bailey, GW, White, JL. Residue Rev. 1970; 32: 29-92.
16. Fushiwaki, Y, Tase, N, Saeke, A, Urano, K. Sci. Otal. Environ. 1990; 92: 55-67.
17. Galvano, F, Pietri, A, Bertuzzi, T, Bognanno, M, Chies, L, De Angelis, A, Galvano, M. J. Food Prot. 1997; 60: 985-991.
18. Abdel-Wahhab, MA, Hassan, AM, Aly, SE, Mahrous, KF. Mut. Res. 2005; 582: 20-27.
19. Gürses, A, Karaca, S, Dogar, C, Bayrak, R, Açıkyıldız, M, Yalçın, M. I. of Colloid and Interface Sci. 2004; 269: 310-314.
20. Nollet, H, Roels, M, Lutgen, P, Meeren, P Van der. , Verstraete, W. Chemosphere 2003; 53: 655-665.
21. Abdel-Wahhab, MA, Nada, SA, Khalil, FA. Anim. Feed Sci. and Tech. 2002; 97:209-219.
22. Carroll, D. Geological Society of America, NY. Special. 1970; Paper, 126.

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