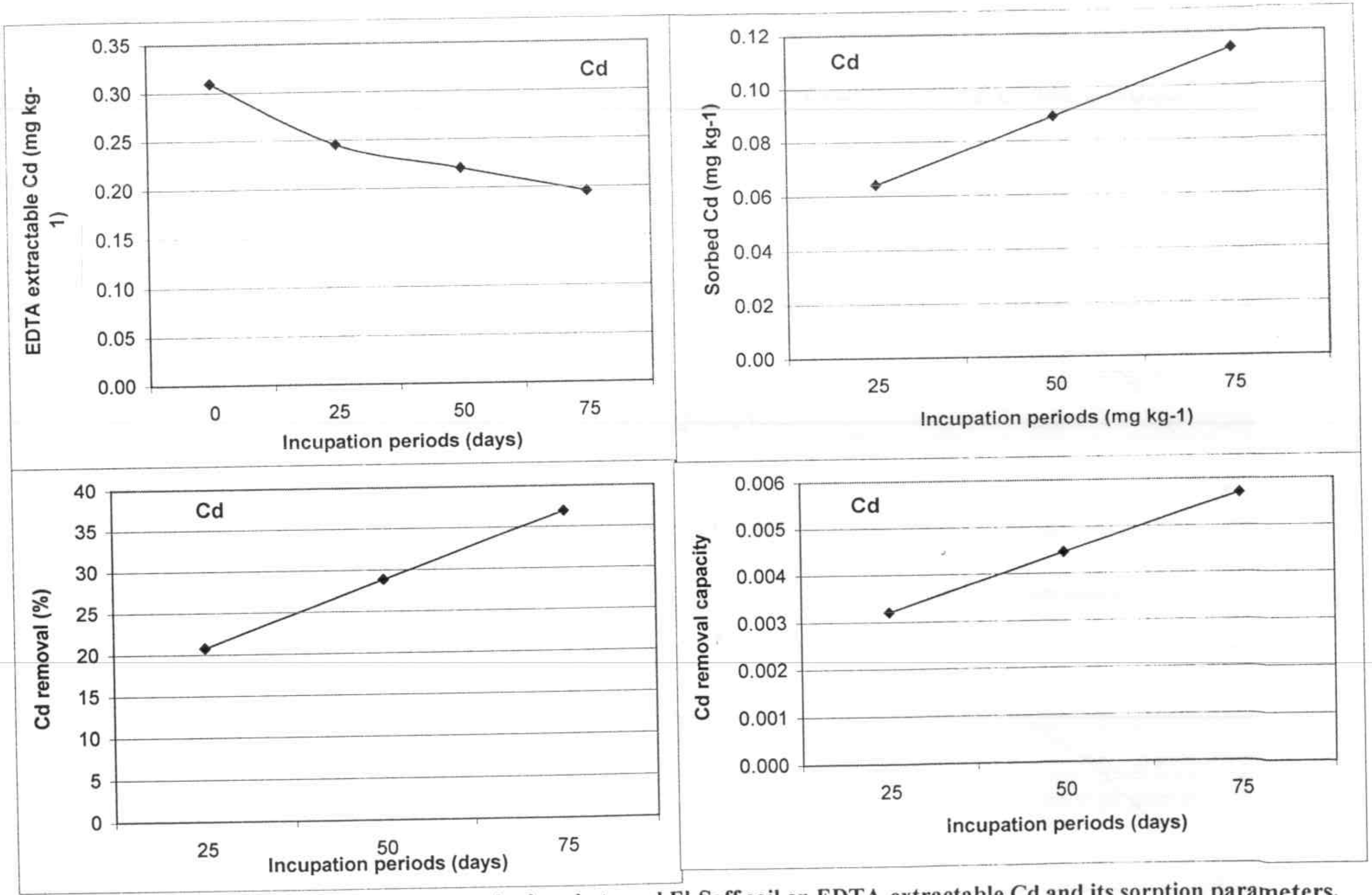


Fig. (24): Effect of time of contact between rock phosphate and El-Saff soil on EDTA-extractable Cd and its sorption parameters.

(removal) percentage in the following descending order: Cd> Ni> Co. This sequence occurred in both the studied soils and for all the studied period of incubation except for the seventy fifth day of incubation in El-Gabal El-Asfar soil with the rock phosphate where the sequence differed slightly where sorption (removal) % of Cd highly exceeded the sorption of Co which slightly exceeded that of Ni. **Christopher *et al.* (2002)** reported that heavy metal ions might exchange with Ca^{2+} (present in rock phosphate) and larger multivalent ions are more effectively removed. Since the investigated metal ions are arranged according to their radii in the following descending order: Cd (0.97 A^0)> Ni (0.69 A^0) > Co (0.65 A^0) accordingly, removal % of these ions should obey the sequence Cd > Ni > Co which was the case in the current study.

Values of the removal capacity i.e. the amount of metal removed per unit weight of the applied adsorbent (rock phosphate) increased with time. This observation was true regardless of kind of the studied soil or metal ion, yet these values were the highest in case of Ni, lowest in case of Co and came inbetween in case of Cd.

The comparison between values of sorption percentage of Ni, Co and Cd between the two investigated soils reveal that El-Gabal El-Asfar amended soil could adsorb higher Ni, Co and Cd values than El-Saff soil at all the incubation periods, however, sorption percentages of these metal ions were relatively higher in El-Saff soil than El-Gabal El-Asfar one except for Cd after 75 days of incubation where its sorption percentage in El-Gabal El-Asfar soil was higher than the corresponding one of El-Saff soil.

As a matter of fact, the initially available EDTA-extractable amounts of Ni, Co and Cd were higher in El-Gabal El-Asfar soil than in El-Saff soils. The higher $CaCO_3$ content of the later soil than the former one may account for such an observation.

Lothenbach *et al.* (1997) went to a similar finding and reported that metal ions solubility in calcareous soils is small. Also, **Robinson *et al.* (2000)** found that $CaCO_3$ significantly decreased the solubility of Ni in soil. **Ismail (2007)** went almost to a similar finding where he found that Ni and Co were sorbed on $CaCO_3$. Also, **Balba (1995)** indicated that heavy metals may react with $CaCO_3$ and precipitate in the form of insoluble heavy metal carbonates.

The higher available contents of Ni, Co and Cd in El-Gabal El-Asfar soil were associated with higher sorption amounts, but at the same time corresponding lower sorption percentages as was cleared by data in Tables (10 and 11) and Figs. (19-24). These results are in accordance with those of **Ismail (2007)** , who found that Ni , Co and Cd desorption values as percentages of their initial concentrations, generally, decreased with increasing their initial concentrations.

The effect of rock phosphate on the amounts of Ni, Co and Cd removed from El-Gabal El-Asfar soil was more obvious, but on the other hand, the sorption (removal) percentages of Ni, Co and Cd were higher in El-Saff soil, probably due to its calcareous nature.

Saxena and D' Souza (2005) although reported that the exact reaction mechanism responsible for removal of metal ions by rock phosphate is unknown, yet they cleared that the sorption process, which, generally, involves species attachment from a solution to the existing solid surface by three types, namely surface adsorption, absorption or diffusion into the solid and precipitation or co-precipitation appears to be governing mechanism for retention of metal ion by rock phosphate.

It is supposed that the primary mechanism of metal ion removal by rock phosphate is governed by its dissolution followed by subsequent precipitations.

Hence, the process may be represented by the following equations:

$$Ca_{10}(PO_4)_6\,F_2 + 12\,H^+ \xrightarrow{\text{dissolution}} 10\,Ca^{2+} + 6H_2PO_4^- + 2F^= \qquad (1)$$

$$10M^{2+} + 6H_2PO_4^- + 2F^- \xrightarrow{\text{Precipitaion}} M_{10}(PO_4)_6F_2 + 12H^+ \qquad (2)$$

In addition to the above hypothesis, where P in the form of $H_2PO_4^-$ helps in precipitation metal ions, the possibility of exchange of Ca by metal ions can not be ruled out **(Perrone *et al.*, 2001)**. It may be interpreted that the dissolution of rock phosphate also provides Ca, which exchanges with aqueous metal leading to the precipitation of corresponding mineral phase. **(Perrone *et al.*, 2001)** reported that there is isomorphic substitution of Ca^{2+} with heavy divalent ions, which is correlated to their ion radii and electro negativity.

4.1.5. Calcium carbonate:-

Data in Tables (12 and 13) and Figs. (25-30) show the effect of the applied $CaCO_3$ as well as its time of contact with both the investigated soils on extractability of Ni, Co and Cd by EDTA and sorption parameters of these elements.

It is obvious that increasing time of contact between $CaCO_3$ and each of the El-Gabal El-Asfar and El-Saff soils reduced progressively amounts of EDTA –extractable Ni, Co and Cd . The reduction amounts of the metal ions seemed highest with Ni, lowest with Co and came in-between with Cd. The reducing effect of $CaCO_3$ on availability of heavy metals was reported by many investigators e.g. **Moore and Loeppert (1990), Nikolov and Zlatareva (2000), Robinson *et al.*(2000) Tadroos (2004) and Ismail (2007)** who found that $CaCO_3$ and pH significantly decreased the extractability of many trace elements in soils among which Ni, Co and Cd.

Table (12): Effect of time of contact between calcium carbonate and Al-Gabal El-Asfar soil on EDTA-extractable ion metals and their sorption parameters

Element	EDTA extractable element (mg kg^{-1})				Sorbed element (mg kg^{-1})			Sorption (removal) %			Removal capacity mg metal ion kg-1 amendment		
	Days												
	0	25	50	75	25	50	75	25	50	75	25	50	75
Ni	4.040	3.909	2.464	2.101	0.131	1.576	1.939	3.243	39.010	47.995	0.007	0.079	0.097
Co	0.078	0.058	0.050	0.046	0.020	0.028	0.032	25.641	35.897	41.026	0.001	0.001	0.002
Cd	0.333	0.234	0.199	0.163	0.099	0.134	0.170	29.730	40.240	51.051	0.005	0.007	0.009

Table (13): Effect of time of contact between calcium carbonate and El-Saff soil on EDTA-extractable ion metals and their sorption parameters

Element	EDTA extractable element (mg kg^{-1})				Sorbed element (mg kg^{-1})			Sorption (removal) %			Removal capacity mg metal ion kg-1 amendment		
	Days												
	0	25	50	75	25	50	75	25	50	75	25	50	75
Ni	1.284	0.860	0.744	0.578	0.424	0.540	0.706	33.022	42.056	54.984	0.021	0.027	0.035
Co	0.123	0.087	0.074	0.068	0.036	0.049	0.055	29.268	39.837	44.715	0.002	0.002	0.003
Cd	0.300	0.189	0.156	0.115	0.111	0.144	0.185	37.000	48.000	61.667	0.006	0.007	0.009

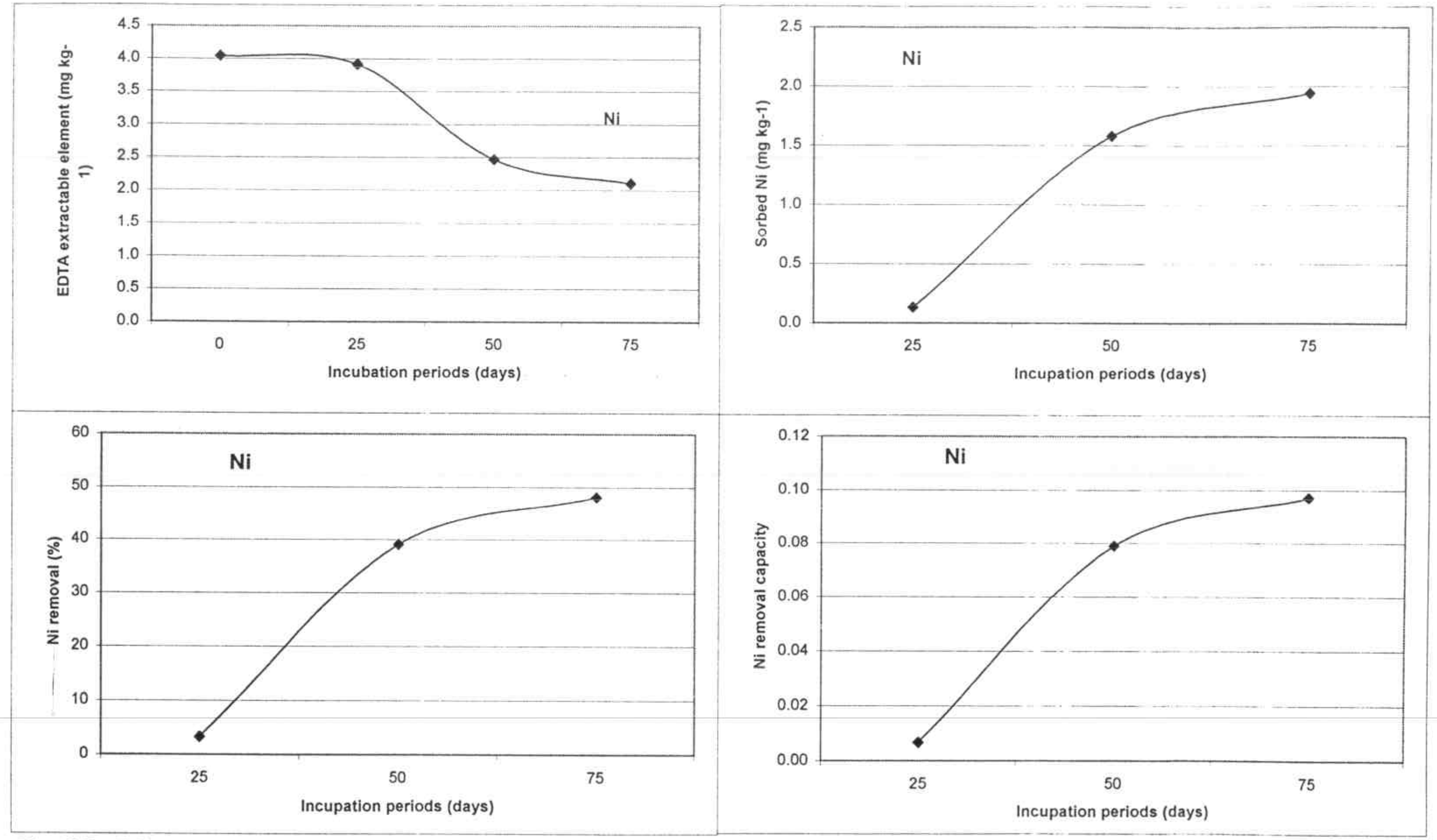


Fig. (25): Effect of time of contact between CaCO3 and El-Gabal El-Asfar soil on EDTA-extractable Ni and its sorption parameters.

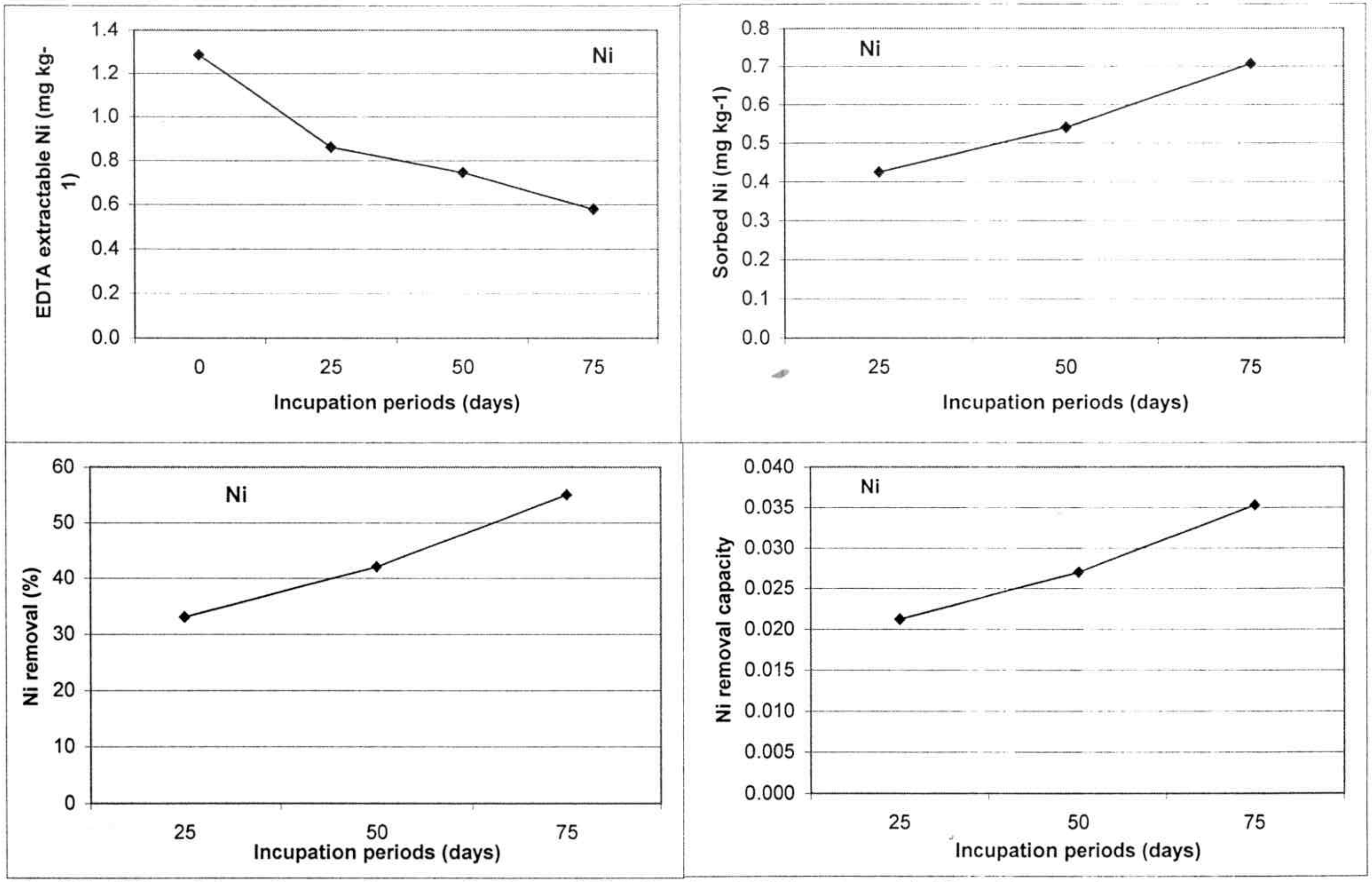


Fig. (26): Effect of time of contact between $CaCO_3$ and El-Saff soil on EDTA-extractable Ni and its sorption parameters.

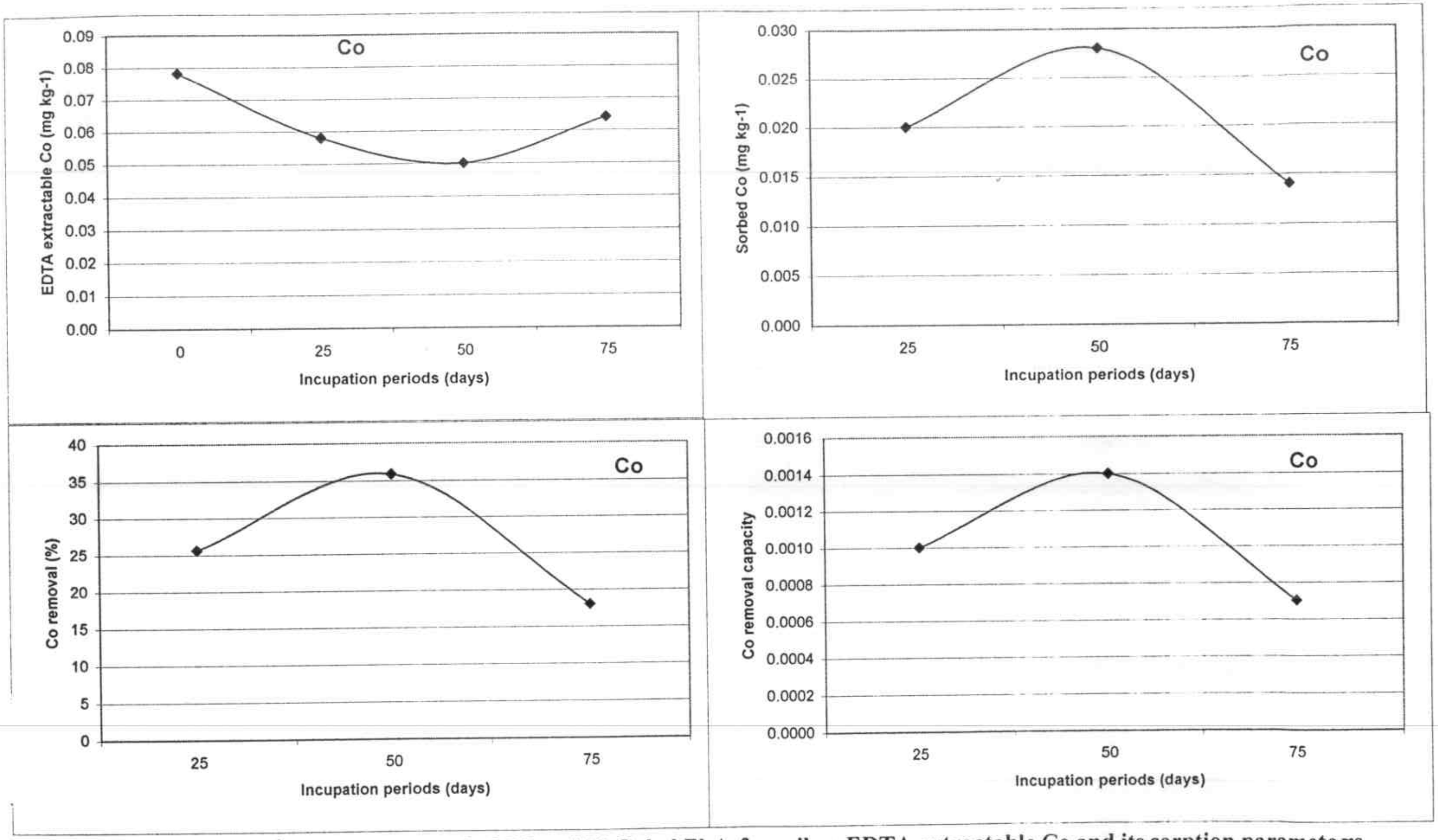


Fig. (27): Effect of time of contact between CaCO3 and El-Gabal El-Asfar soil on EDTA-extractable Co and its sorption parameters.

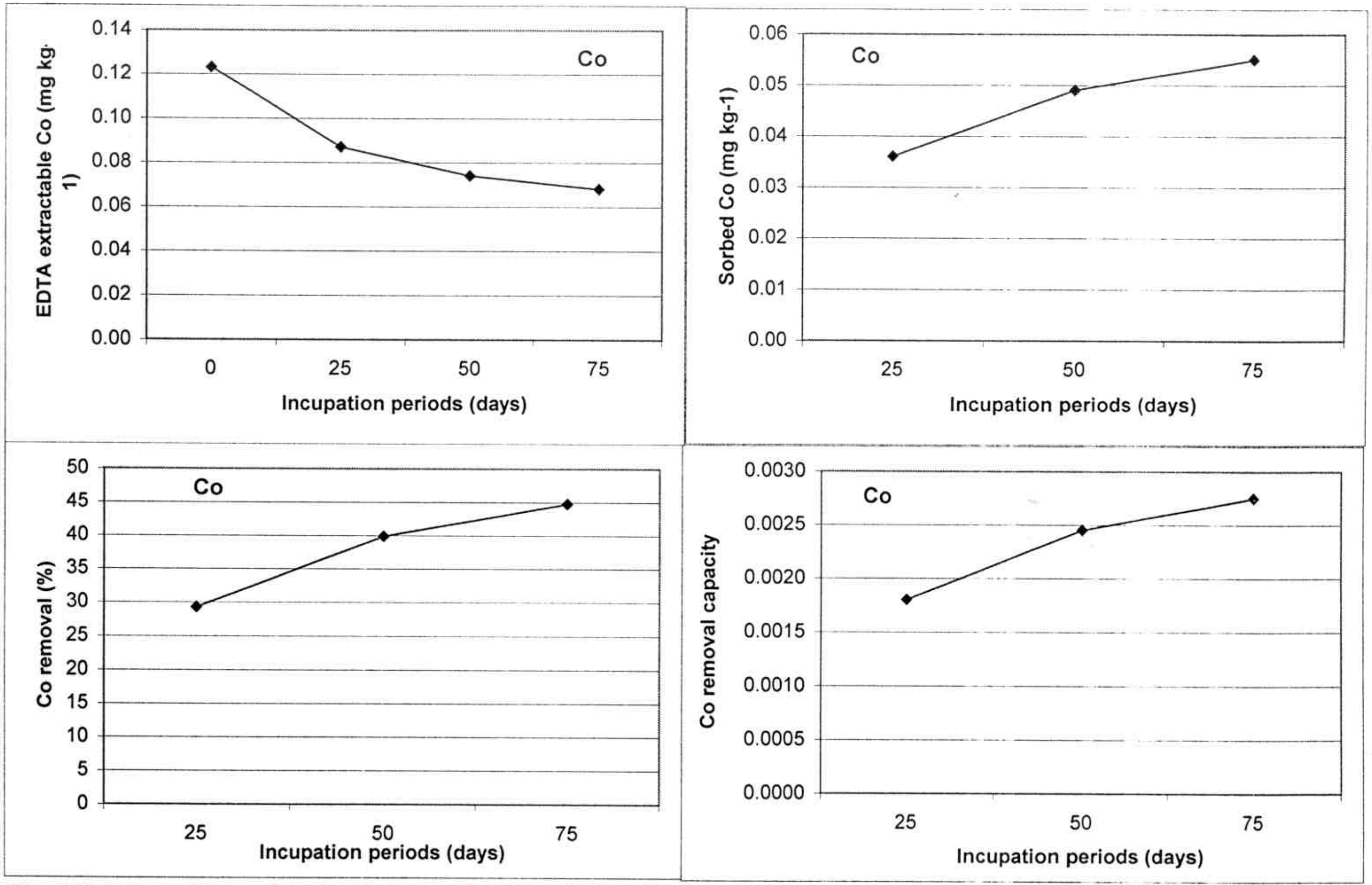


Fig. (28): Effect of time of contact between CaCO3 and El-Saff soil on EDTA-extractable Co and its sorption parameters.

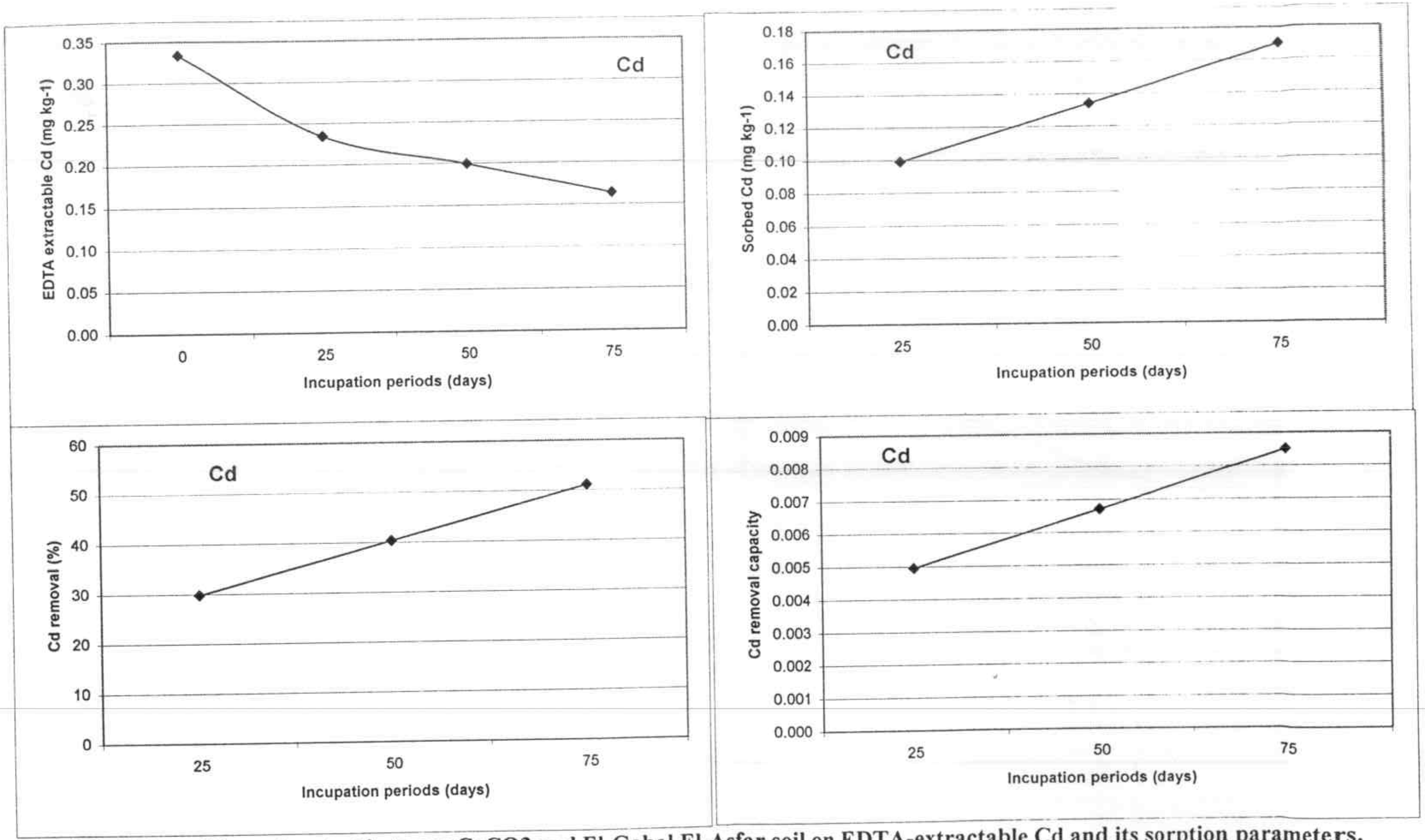


Fig. (29): Effect of time of contact between CaCO3 and El-Gabal El-Asfar soil on EDTA-extractable Cd and its sorption parameters.

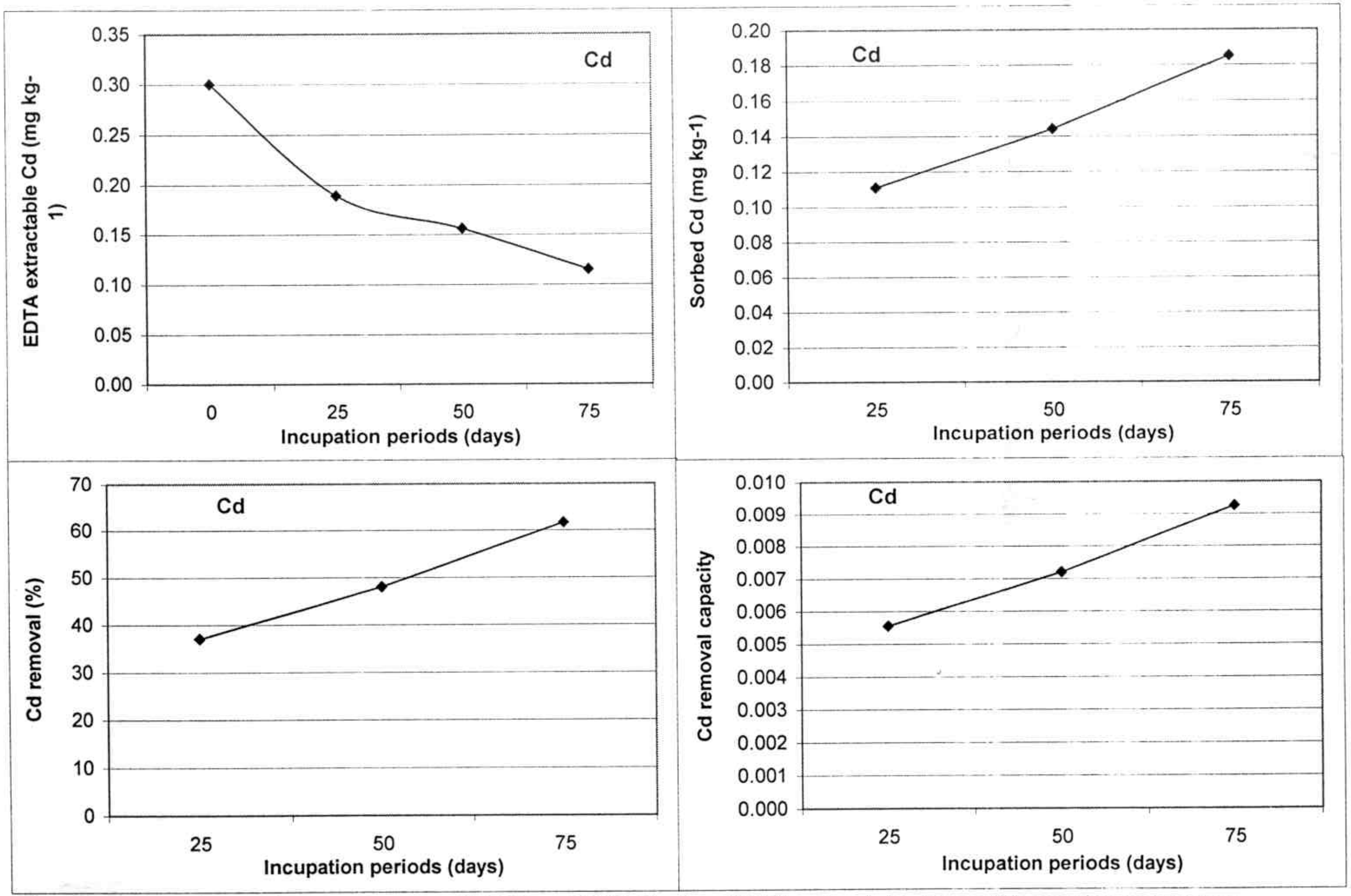


Fig. (30): Effect of time of contact between CaCO3 and El-Saff soil on EDTA-extractable Cd and its sorption parameters.

Balba (1995) reported that the decrease in trace metals availability upon application of $CaCO_3$ to soil is mainly related to the increase in soil pH resulting from hydrolysis of $CaCO_3$ which yields OH^- ions as follows:-

$$CaCO_3 + H_2O \rightarrow Ca^{2+} + HCO_3^- + OH^-$$

Kabata- Pendias and Pendias (1992) reported that solubility of most metal ions will decrease with increasing soil pH. This observation can be explained by the precipitation of metal hydroxides.

Sorbed amounts (mg kg^{-1}) of the concerned metal ions increased with increasing time of contact between soils and $CaCO_3$. Over all periods of incubation sorbed amounts of the studied metal ions followed the descending order : Ni > Cd > Co regardless of type of soil. This sequence agrees, to a great extent, with the concentrations of the studied metal ions in both the investigated soils at zero time of incubation whose they followed the same aforementioned sequence i.e. Ni > Cd > Co.

This finding stands in well agreement with the results of **Ismail (2007)** who found that adsorbed amounts of Ni and Co on $CaCO_3$ increased progressively with increasing concentrations of the concerned metal ions in the equilibrium solution.

It is worthy to indicate that after 25 days of incubation,sorbed amounts of Ni, Co and Cd on El-Gabal El-Asfar soil were lower than the corresponding amounts sorbed on El-Saff soil although the initial concentrations of these metal ions in the former soil were obviously higher than the corresponding ones of the latter. After 50 and 75 dayes of incubation,sorbed amounts of both Co and Cd on $CaCO_3$ – amended soil of El-Saff exceeded the corresponding amounts of metals sorbed on $CaCO_3$ – amended soil of El-Gabal El-Asfar. In both these periods, sorbed Ni followed an opposite trend where it was found in El-Gabal El-Asfarsoil in higher amounts than in El-Saff soil. The higher original content of $CaCO_3$ in El- Saff soil might participate with the $CaCO_3$ applied as an amendment in sorption of the concerned metal ions. Therefore, sorpation (removal) percentage values of the metal ions in El-Saff soil, generally, exceeded the corresponding sorption percentage ones in El-Gabal El-Asfar soil. However, in both soils sorption percentage values of the metal ions tended to increase by prolonging period of incubation.

Values of removal capacity increased also with time and seemed to be in the descending order: Ni > Cd > Co. **Guo *et al.* (2006)** reported that it is a common practice to apply lime to reduce the extractable metal concentration and successfully immobilize heavy metals in soils. They added that $CaCO_3$ may reduce trace elements solubility in two ways:-

(1) It raises the soil pH and

(2) it adsorb trace element ions.

4.2. Effect of treating El-Gabal El-Asfar and El-Saff wastewater with different algae species on their residual contents, removed amounts and removal percentage of Cd, Co and Ni:

The accumulation of heavy metals by algae in laboratory media has been in the focus of numerous studies, where some micro algae spices can be used for removal of heavy metals from industrial-waste solutions (**Ross, 1980**). The presence of heavy metals in the environment is partially due to natural processes, but is mostly the result of industrial waste (**Mansour and Sidky, 2002**). Contamination of aquatic ecosystems with heavy metals has increased worldwide.

4.2.1. Cadmium:

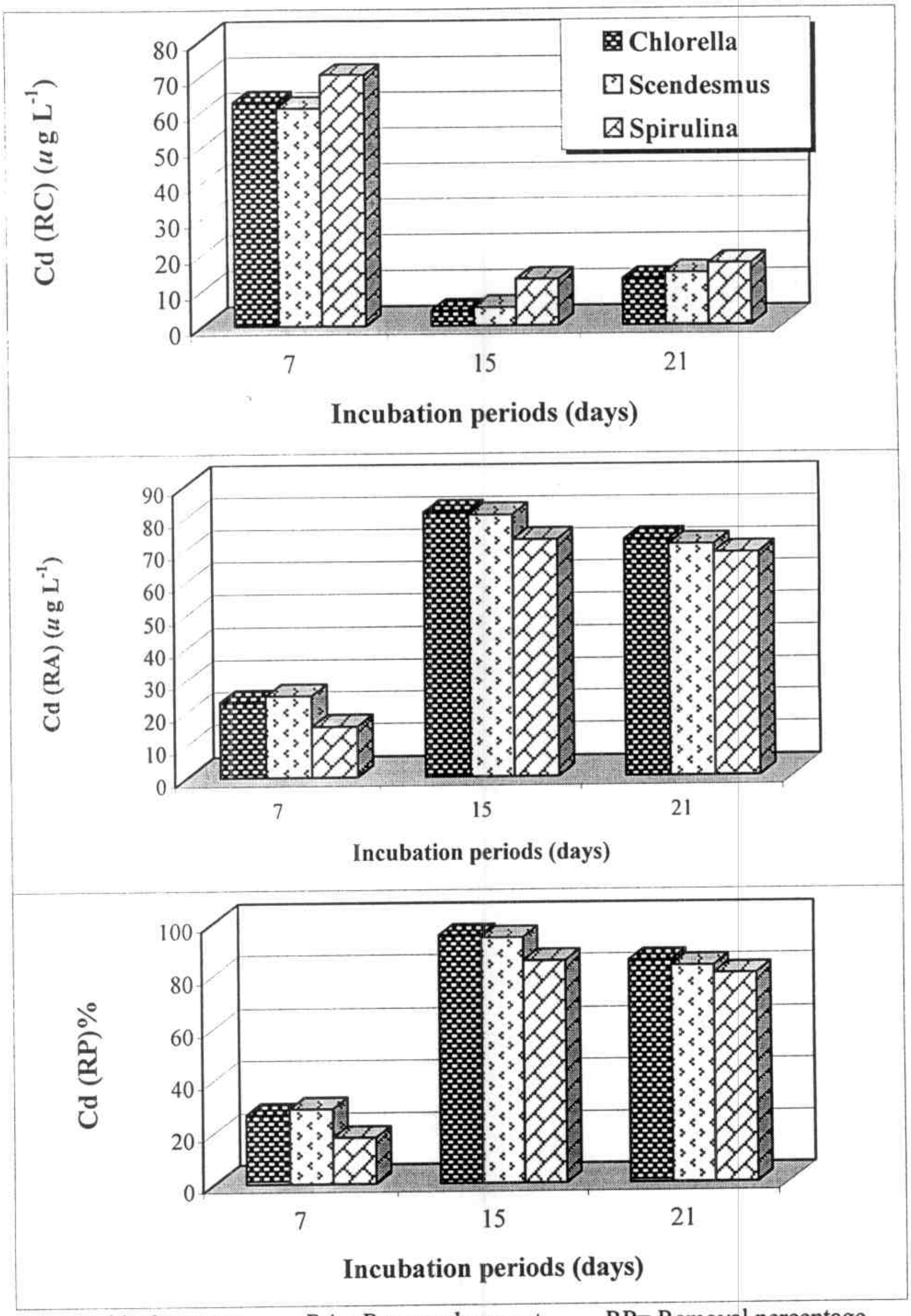
Cadmium (Cd) is a toxic heavy metal, a contaminant mainly of aquatic ecosystems. It has many industrial uses, such as in Cd batteries, anti-corrosive coating of metals, pigments, and stabilizers for plastic **(Stoeppler, 1991)**. The amount of Cd used in industry is increasing.

Data in Table (14) and Fig. (31) show the residual content (RC), removed amount (RA) of heavy metals (µg /L) and removal percentage of elements (RP) of wastewater of El-Gabal El-Asfar treated with algae during different incubation periods.

The removed amounts of Cd by algae during the studied different incubation periods i.e. 7, 15 and 21 day were 23.22, 81.70 and 73.10 µg/L for *Chlorella vulgaris*, 24.94, 80.84 and 71.38 µg/L for *Scenedesmus obliquus* and 15.48, 73.10 and 68.80 µg/L for *Spirulina platensis* respectively. The minimum removed value of Cd from media (15.48 µg/L) was recorded at the first period by *Spirulina*, while the maximum (81.7 µg/L) was recorded by *Chlorella* at the second incubation period.

Table (14): Effect of treating El-Gabal El-Asfar wastewater with different algae species on its content of cadmium under different incupation periods.

Type of wastewater	Periods (day)	Cd Status	Chlorella	Scenedesmus	Spirulina
	0	Initial Concentration µg/L (IC)	86.00	86.00	86.00
El-Gabal E-Asfar wastwater experiment	7	Residual Content (RC) µg/L	62.78	61.06	70.52
		Removed Amount (RA) µg/L	23.22	24.94	15.48
		Removal Percentage (RP) %	27.00	29.00	18.00
	15	Residual Content (RC) µg/L	4.30	5.16	12.90
		Removed Amount (RA) µg/L	81.70	80.84	73.10
		Removal Percentage (RP) %	95.00	94.00	85.00
	21	Residual Content (RC) µg/L	12.90	14.62	17.20
		Removed Amount (RA) µg/L	73.10	71.38	68.80
		Removal Percentage (RP) %	85.00	83.00	80.00
Mean		Removed Amount (RA) µg/L	59.34	59.05	52.46
		Removal Percentage (RP) %	69.00	67.00	53.67



RC= Residual content, RA= Removed amount, RP= Removal percentage

Fig. (31): Effect of treating El-Gabal El-Asfar wastewater with different algae species on its content of cadmium under different incubation periods.